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**United States Patent** [19][11] **Patent Number:** **5,922,903****Pujado**[45] **Date of Patent:** **Jul. 13, 1999**[54] **FALLING FILM REACTOR WITH CORRUGATED PLATES**[75] **Inventor:** Peter R. Pujado, Kildeer, Ill.[73] **Assignee:** UOP LLC, Des Plaines, Ill.[21] **Appl. No.:** 08/967,137[22] **Filed:** Nov. 10, 1997[51] **Int. Cl.<sup>6</sup>** ..... C07C 303/26; C07C 41/03[52] **U.S. Cl.** ..... 562/98; 562/95; 562/123;  
568/608; 568/618; 568/648; 568/670; 568/678;  
568/679; 422/198; 159/47.1[58] **Field of Search** ..... 562/98; 123, 608;  
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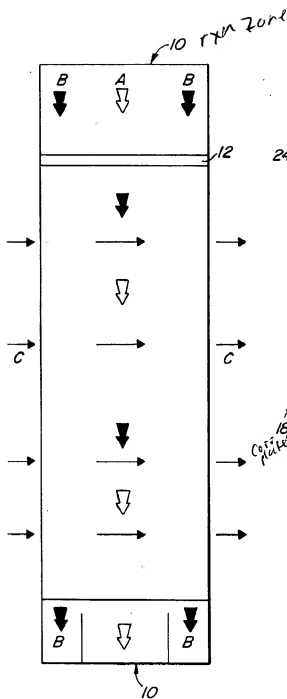
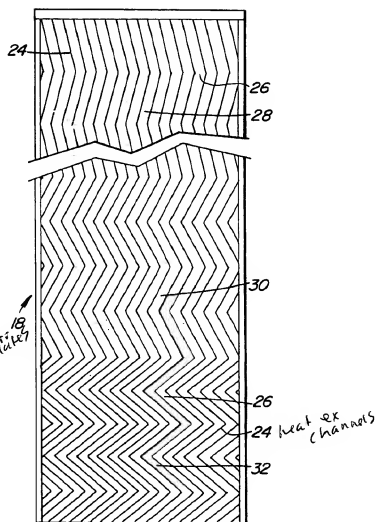
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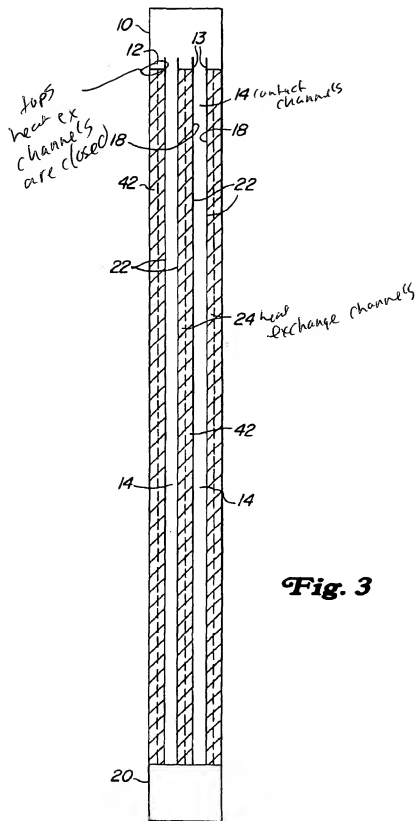
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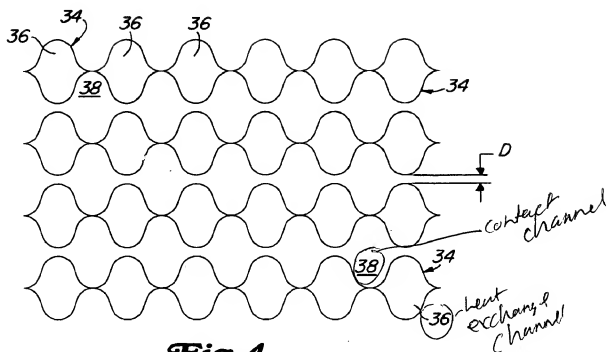
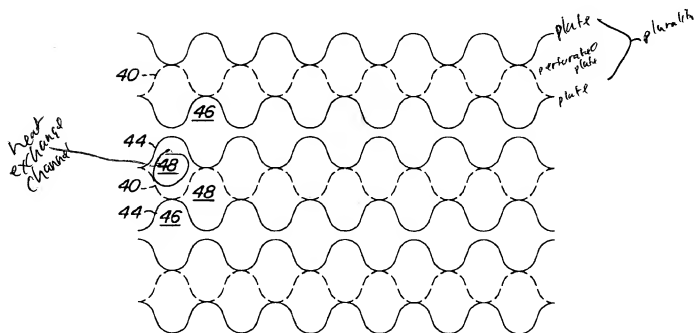
**ABSTRACT**

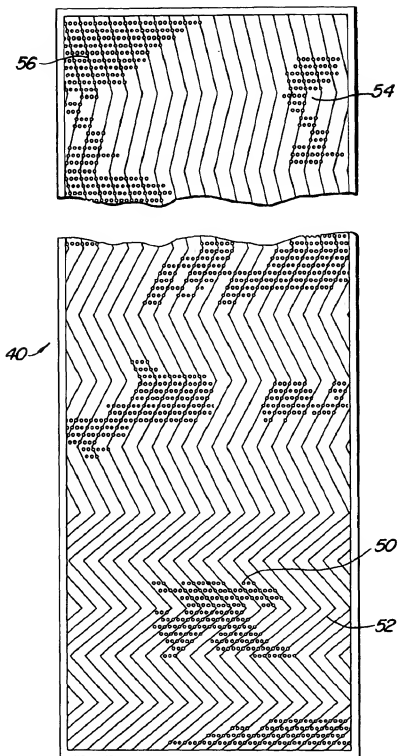
An arrangement for a falling film type reactor uses corrugated plates to improve the distribution and dispersion of the gaseous reactant into the liquid. Corrugated plates introduce increased turbulence for promoting better distribution and dispersion of the gas. Corrugation angles can be varied to suit the fluid flow properties of the liquid reactant. The reactor arrangement can also include heat transfer channels defined by the corrugated plates in an alternate arrangement of heat transfer channels and gas liquid contacting channels. The corrugations may also be varied to suit the particular heat transfer requirements of the reactions. The corrugated plates are spaced apart in the contacting channels to prevent localized film contact and placed in contact in the heat exchange portion to stabilize the plate elements defining the corrugations.

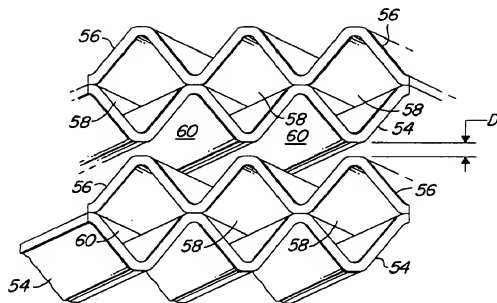
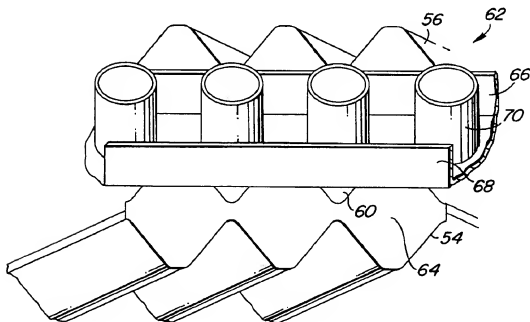
**12 Claims, 5 Drawing Sheets**

**Fig. 1****Fig. 2**

**Fig. 3**

**Fig. 4****Fig. 5**

**Fig. 6**

**Fig. 7****Fig. 8**

# FALLING FILM REACTOR WITH CORRUGATED PLATES

## FIELD OF THE INVENTION

This invention relates generally to the interaction of a thin film of a liquid stream with a gaseous stream as the liquid passes down contacting surface. More specifically this invention relates to plate structures for vertical falling film contacting or removal of gaseous streams.

## BACKGROUND OF THE INVENTION

Falling film evaporators and reactors are well known in the art and are readily available commercially. Falling film evaporators pass a thin film of a liquid stream down one side of a heat exchange surface in indirect heat exchange with a heating medium that contacts an opposite side of the heat exchange surface and causes an at least partial evaporation of the falling liquid. Falling film reactors comprise a plurality of tubes or plates over which a thin film of one reactant is dispersed for countercurrent or concurrent contact with a gaseous reactant stream. In the case of evaporation or reaction laminar flow layers in the thin film can inhibit heat transfer and diffusion of vapor.

One of the most well known falling film reactor arrangements is for the continuous sulfonation or sulfation of fluid state organic substances by reaction with sulfur trioxide (sulfuric anhydride) ( $\text{SO}_3$ ). In falling film arrangements, the  $\text{SO}_3$  or other reactant is kept in a gaseous state. The reaction of the  $\text{SO}_3$  with the organic substances is strongly exothermic throughout the reaction which occurs rapidly or in many cases goes nearly instantaneously to completion. The  $\text{SO}_3$  is normally diluted with air or other inert gases to a reduced concentration of 4-15 wt % which attenuates the severity of the reaction. The provision of cooling to the falling film contact surfaces also avoids the generation of temperature peaks from the highly exothermic reaction.

U.S. Pat. No. 3,925,441 issued to Toyoda et al. describes the use of flat plates for falling film sulfonation.

U.S. Pat. No. 5,445,801 to Pisoni describes a tube arrangement for falling film sulfonation that provides improved liquid distribution and accommodates expansion of the tubes.

U.S. Pat. No. 4,059,620 issued to Johnson describes the advantages of maintaining a desired heat exchange profile during the sulfonation of organic compounds with sulfur trioxide.

The sulfonation or reaction of other organic compounds can cause extensive side reactions. Side reactions are best minimized by a uniform distribution of liquid and gaseous reactions over contact surfaces. Systems for controlling the distribution into tubes or plate arrangements for falling film reactors include: weir and dam systems and slit or orifice arrangements that can be mechanically adjusted in various ways. Nevertheless, minor irregularities in the delivery systems to the top of the falling film apparatus can result in substantial flow variations with the attendant drawback of side reaction production. In addition to the problems associated with uniform delivery to a falling film contact surface, variations in the surface also create flow irregularities that can lead to non-uniform contacting and promote side reaction production.

Therefore, a reactor system is sought that will eliminate boundary layer limitations in falling film evaporators or contactors, overcome initial mal-distribution of liquid reactants in a falling film contactor and maintain an equalized

distribution of reactants in a uniform film over the contact surface of the reactor.

## SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide an apparatus and process for a falling film contacting surfaces that continually redistributes the liquid film.

Another object of this invention is to provide a falling film reactor arrangement that promotes dispersion of the gaseous reactant through the thin film of liquid.

A yet further object of this invention is to provide a falling film process and arrangement that facilitates indirect heat transfer between the falling film and a heat transfer medium.

These and other objectives are achieved by a falling film device that distributes a liquid stream to a plurality of corrugated contacting columns defined in a vertical arrangement of contacting plates. The corrugations are arranged to have a primary axis that extends at least partially in a direction transverse to the vertical flow of the falling film. Movement of the fluid over the transversely extending corrugations introduces turbulence that disperses the gaseous reactants through the fluid stream for thorough and uniform contacting. Multiple corrugated plates are spaced apart across falling film contacting channels by a distance sufficient to prevent contacting of the falling film with the adjacent plates. A heat transfer fluid may be circulated to contact the sides of the corrugated plates opposite the falling film and thereby provide cooling or heating to the liquid for temperature control. Turbulence introduced by the corrugated plates will again facilitate the indirect heat transfer between the liquid film and the heat transfer medium. In this manner the corrugated plate arrangement provides advantages for the dispersion, contacting and cooling of liquid and gases in a falling film contactor arrangement.

Accordingly, in a broad process embodiment, this invention comprises a process for the contacting of a thin film liquid stream with a gaseous stream. The thin film stream passes down a plurality of corrugated surfaces defined by a plurality of vertically oriented plates. A space sufficient to prevent direct contact between adjacent films separates the adjacent plates over which the thin films descend. A gaseous stream passes through the vertical channels between the adjacent plates for dispersion into or out of the film. The process recovers a process stream from the bottom of the plates.

In another process embodiment, this invention comprises a process for the reaction of a thin film liquid stream with a gaseous reactant. The thin film stream passes down a plurality of corrugated surfaces defined by a plurality of vertically oriented plates. A space sufficient to prevent direct contact between adjacent films separates the adjacent plates over which the thin films descend. A gaseous reactant stream passes upwardly through the vertical channels between the adjacent plates for dispersion into the film. The process recovers a reaction product from the bottom of the plates.

In a more specific process embodiment, the process sulfonates organic substances by passing a stream comprising an organic liquid as a plurality of thin films down corrugated surfaces defined by a plurality of vertically oriented plates. A spacing sufficient to prevent direct contact between the films separates adjacent plates. A gaseous stream containing sulfur trioxide passes through the open vertical channels defined by the vertical plates for dispersion within the thin film. An effluent from the plates comprising a sulfonated reaction product is recovered at the bottom of the channels.

In an apparatus embodiment, this invention comprises a falling film contactor that contains a plurality of corrugated plates positioned in a parallel arrangement to define contacting channels between the adjacent plates. The plates define corrugations that extend at least partially in a horizontal direction. The adjacent plates over which the film passes have sufficient spacing to prevent contacting of liquid films passing over the surface of the adjacent plates. A distribution means provides a uniform distribution of liquid from the tops of the plates over the corrugated surfaces. An additional distribution means receives a gaseous stream through the contacting channels for dispersion into or out of the liquid descending along the plates. Means at the bottom of the plates collect a liquid stream from the contacting channels.

The process and apparatus will ordinarily employ a heat exchange fluid to control the temperature of the reactants in the falling film contactor. The heat transfer fluid passes through channels defined by the opposite side of the contacting plates over which the thin film passes. The degree of heat transfer occurring over the heat transfer surface may be varied by inclining heat transfer plates between contacting plates. The pitch and number of corrugations on the heat transfer plates may vary over the length of the plates and may vary with respect to the corrugations on the contacting plates to enhance and control heat transfer over the length of the contacting plates.

The arrangement of the corrugations of the contacting plates can be varied to suit the particular characteristics of the process and fluids employed. For low surface tension and low viscosity fluids, a relatively horizontal and shallow pitched corrugation is most beneficially employed. A slight downward pitch may be provided on the horizontal corrugations to provide a transverse movement of liquid and its redistribution as it travels down the reactor. The corrugation sections are preferably in a herring bone pattern so that the fluid flows back and forth in a horizontal direction across the reactor as it moves downwardly over the reactor thereby increasing the redistribution and uniformity of the downward flow. The number and height of corrugation rows can be varied in order to increase the dispersion of liquid reactant descending the corrugations. As the viscosity or surface tension of the liquid reactants in the film increases, the slope of the corrugations and depth of the corrugations may be increased to provide additional redistribution and turbulence. Preferably, any intersection or discontinuity points between corrugations are staggered horizontally to prevent collection and vertical channeling of liquid at corrugation valleys.

Additional details, embodiments, and arrangements of this invention are described in the following "detailed description of the invention."

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing a plate reactor of this invention and the direction of process flow streams.

FIG. 2 is a schematic diagram of a corrugated plate for the liquid gas contacting of this invention.

FIG. 3 is a schematic cross-section of a falling film reactor arranged in accordance with this invention.

FIG. 4 is a schematic cross-section of a contactor channels arranged in accordance with this invention.

FIG. 5 is a schematic cross-section of a modified contactor channel section arranged in accordance with this invention.

FIG. 6 is a schematic diagram of a perforated plate for the heat transfer channels of this invention.

FIG. 7 is a three-dimensional view of a portion of the contacting and heat exchange channels of this invention.

FIG. 8 is a three-dimensional view of a liquid distribution system for supplying liquid to the top of the contacting channels.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention is broadly applicable to any system in which liquid and gas contacting takes place by the formation of a thin film layer upon a contact surface and the diffusion of the gas about the liquid. The contactor may operate as a reactor or an evaporator.

The turbulence induced by the corrugations for the liquid flow may also be useful in the design of falling film evaporators. The turbulence induced by the corrugations can maintain mixing as the fluid flows to overcome laminar flow characteristics that give rise to temperature concentration gradients in the film. The turbulence induced by the corrugations will allow the enriching capacity of the evaporation to continue at high efficiency over the entire length of the contacting surface.

Another highly beneficial use of the reactor arrangement of this invention is in its use as an ethoxilation reactor. In such reactions, the material to be ethoxilated such as an alcohol or an alkylphenol flow down a surface as a thin film layer. Ethylene oxide is circulated as a gas in a concurrent or countercurrent direction. Close temperature control in such reactions is desired to prevent the formation of unwanted side products. The use of the corrugations of this invention in a flat plate surface promote liquid turbulence and overcome the laminar nature of the flow which induces severe temperature and concentration gradients across the thin film.

The most common example of a reaction system is a sulfonation process which is meant to designate any procedure by which a sulfonic acid group with a corresponding salt or sulfonal halide is attached to a carbon atom. The sulfonation method for which this invention is most broadly suited is the treatment of an organic compound with a gas phase sulfur trioxide. Common starting compounds for this sulfonation reaction include alkyl olefins having 8-30 carbon atoms, alkyl benzenes having 8-15 carbon atoms, and aliphatic alcohols having 8-24 carbon atoms.

The organic compounds enter the reactor in a liquid phase and form a falling thin film in the reaction zone. Typical temperatures for the falling film reactant materials are in the range of 10-45° C. although actual temperatures may vary substantially with the organic material.

The SO<sub>3</sub> reactant is introduced into the reaction zone in combination with an inert gas in a concentration of from 1-20 wt %, and preferably, it is introduced in a concentration of from 3-15 wt %. Concentrations greater than 20 wt % are not desirable since the high concentration will introduce temperature peaks associated with instantaneous sulfonation of the hydrocarbon reactants as they enter the contacting channels.

The general operation of the contactor of this invention may be more fully appreciated from the drawings. FIG. 1 shows a generalized flow arrangement for a falling film liquid reactant and a gaseous reactant that undergoes simultaneous cooling by indirect heat exchange in a reaction zone. FIG. 2 schematically shows a typical corrugated plate 18 which in combination with other plates define contacting channels 14 and heat exchange channels 24 as more fully shown in FIG. 3. The liquid, designated by stream B enters the top of the reaction zone and is distributed to the sides of



the contacting channels by weirs 12 as shown in FIGS. 2 and 3. Liquid enters the weir system 12 that distributes the liquid across the length of the contacting channel 14. Liquid for distribution down the side of the reactor collects in the weirs defined by dam plates 13 and the closed tops of heat exchange channels 24. Liquid over flowing the weir creates a uniform film passing down the sides 16 of a corrugated plate 18.

The gaseous reactant, shown by stream A in FIG. 1, enters the top of reactor 10 and flows freely down the contacting channels and diffuses into the liquid as it falls over the contacting surface 18. Gas disengages from the liquid in the bottom 20 of reactor 10 for collection of the product stream and recovery and recycle of the gas. The gas phase reactant will usually flow concurrently with the liquid reactant. However, the gas phase reactant may be introduced to the system for cocurrent, countercurrent or cross-current flow.

As shown by FIG. 3, the tops of the heat exchange channels 24 are closed to liquid and gas flow to provide a sealed space for isolated transfer of the heat exchange fluid. The heat exchange fluid is most simply passed through the reaction zone in a transverse direction with the liquid reactants. Suitable manifold structures can distribute and collect the heat exchange fluid from the multiple heat exchange channels at the sides of the reaction zone. Alternatively, suitable manifold arrangements for distributing and collecting the heat exchange fluid in a cocurrent or countercurrent flow direction with respect to the liquid reaction are also known.

It is essential to this invention that the plates defining the contacting channel have corrugations formed in their surface. The corrugation pattern for a typical plate 18 as shown in FIG. 2 may be uniform throughout or may vary down the length of the plate as shown in FIG. 2. FIG. 2 shows the corrugation patterns in the idealized fashion with solid lines 24 for the ridges of the corrugations and centralized valley portions 26 between ridges 24.

Suitable heat exchange and contacting plates for this invention will comprise any plates which are easily secured in the reaction section in a stable configuration that readily retains the corrugated arrangement. The plates may be formed into curves or other configurations, but flat plates are generally preferred for stacking purposes. Thin plates are ordinarily used and typically have a thickness of from 1-2 millimeters. The plates are typically composed of ferrous or non-ferrous alloys such as stainless steels. The general herring bone pattern on the faces of the opposing corrugated plates preferably extends in opposite directions such that the opposing plate faces may be placed in contact with each other to form the flow channels and provide structural support to the plate sections.

The corrugation pattern may be varied to achieve a variety of contacting and reaction effects. Such effects include increased turbulence for improving the contacting between the falling film and the gas phase components and varying the pitch of the corrugation to influence the velocity of the falling liquid as it passes downwardly over the ridges of the corrugations. For example, where rapid heat exchange is desired, the corrugations may extend substantially longitudinally with respect to the fluid flow as shown by section 28 of the drawing. As less cooling is needed, the ridges of the corrugations can be made more transverse to the flow to impede the flow thereby increasing the residence time of the falling film as more of the reaction is completed and less heat is generated. The reduced vertical run and increased pitch for each section of corrugation increases the turbulence

of the flowing liquid and improves the diffusion of the gaseous reactant through the liquid reactant.

The transverse component of the ridges may increase continually or in the stepwise fashion as shown in FIG. 2 by sections 28, 30, and 32. As shown by FIG. 2, the channels defined by the corrugations generally run in a generally vertical direction. Chevron type corrugation arrangements that extend in a substantially horizontal direction should be avoided to prevent concentration of the liquid at the bottom points of the corrugation intersections. The arrangement of vertically continuous flow paths as shown in FIG. 2 keeps the liquid stream dispersed and avoids localized concentration of the liquid.

The degree of turbulence may also be controlled by varying the amplitude of the corrugations and the frequency of the corrugations, which are otherwise referred to as the pitch and the depth of the corrugations. Corrugations having a large pitch or low frequency and shallow depth or low amplitude will provide a low degree of turbulence. Increasing either or both of the frequency and amplitude will raise the degree of turbulence.

It is also essential to this invention that the peaks and valleys of the corrugations defined by adjacent plates are spaced apart by a sufficient distance to prevent substantial contact of the fluid films. Contact between the fluid films as they descend down the plates can cause localized pooling of reactants and undesirable variations in residence time and reactant temperatures. The obstructions formed by the contact of film layers will retard the flow in those film portions through surface tension and frictional losses.

The corrugated plates will usually define heat exchange channels on the side opposite to the film. The heat exchange channels will normally contain a heat exchange fluid. The heat exchange fluid can comprise any fluid having the desired heat exchange and fluid flow characteristics. Plates defining the heat exchange channels preferably contact each other at the high points of the corrugations. Arranging the corrugations in contact, promotes structural stability and support for the heat exchange plates.

FIG. 4 schematically depicts plates 34 into which corrugations are formed for defining heat exchange channels 36 and contacting channels 38. FIG. 4 shows the preferred arrangement where plates 34 are placed to contact adjacent corrugations in the heat exchange channels 36 while the corrugations in the contacting channels 38 are placed apart by a distance D. The distance D will vary depending on the process conditions and the properties of the liquid. The distance D will typically equal at least twice the maximum film layer expected during the operation of the process. Spacing D may be maintained by use of occasional spacers that contact the points of the corrugations. Such spacers may consist of thin pins that extend over the entire vertical length of the contacting channels or thin bars that extend transversely across the contacting channels.

Flow variations induced by the corrugation pattern can be independently controlled in the contacting channels versus the heat exchange channels. In particular it may be beneficial to vary the turbulence effect related to the corrugation pattern in the heat exchange channels separately from that of the contacting channels. As shown schematically in FIGS. 3 and 5, this may be accomplished by inserting an additional plate 40, 42, within the heat exchange channels. As shown schematically in FIG. 3 such an arrangement sandwiches plate 40 between plates 44 within heat exchange channels 46. The heat exchange insert plate may be a flat plate with a turbulence inducing structure shown in the U.S. Pat. No.

5,538,700 or a corrugated plate as schematically depicted in FIG. 5. As more clearly illustrated in FIG. 6, the corrugated plate preferably contains perforations 50 between ridges 52 and valleys 54 of the corrugations 56.

The use of the heat exchange insert plate has the additional advantage of facilitating the use of horizontal corrugations in the contacting channels. When the plates define horizontal corrugations they cannot be placed in contact with each other in the heat exchange channels without blocking flow. Not placing the plates in contact results in a weakened structure. The insertion of a perforated plate between horizontal corrugations maintains the channel for the heat exchange fluid in the heat exchange channel and allow all of the plates to be in contact in the heat exchange channels for improved structural stability.

The preferred arrangement of the corrugated plates with a herring bone pattern extending in different directions is more clearly depicted in FIG. 7. Corrugated plates 54 slope generally to the left as they extend downward while corrugated plates 56 extend transversely to the right as they slope downward. Corrugated plates 56 and 54 are placed in contact with each other on one side to define the heat exchange channels 58. On opposite sides corrugated plates 54 and 56 are again spaced apart by distance D and form the contacting channels 60.

FIG. 8 shows one arrangement for a weir system 62 arranged at the top of the corrugations 54 and 56. The weir system distributes liquid to the tops of the corrugation valleys while they also provide open area for gas flow into the channels. The tops of the heat exchange channels defined by plates 54 and 56 are closed by appropriate plugs or seals over the area depicted by numeral 64. The channel system 66 extends over the center of the contacting channels for distributing liquid thereto. The width of liquid channel 66 is less than the width of the contacting channels such that the outermost ends of the channel are left open for fluid to enter the tops of the contacting channels. Liquid overflows the top of channel sidewalls 68 and flows into the outermost section of channel 60. The downward slope of the corrugation distributes liquid as it contacts the angled surface of the corrugations defined by plates 54 and 56. Gas flow into the contacting channels is maintained through the open outer portion of contacting channel 60 and gas risers 70 that extend upwardly from the liquid distribution channel 66. Gas risers 70 are located above the level of side plate 68 to prevent liquid from flowing therein.

#### Illustrative Embodiment

This invention can be used to operate an isothermal sulfonation process for the sulfonation of an alpha olefin with sulfur trioxide. In such an arrangement, an alpha olefin stream comprising olefins having from 15-18 carbon atoms is formed into a thin film stream by the use of a falling film distributor as depicted in FIG. 8. A stream of SO<sub>3</sub> and air flows parallel to the alpha olefins through the contacting channels to effect a reaction. The velocity of the air and SO<sub>3</sub> stream is about the same as that of the liquid flowing through the contacting channels. The SO<sub>3</sub> containing air stream contains about 7.3 vol. % SO<sub>3</sub> and passes through the reactor at a velocity of about 65 m/sec. The film stream passing over the plates is maintained at a temperature of about 50° C while cooling water passes through the heat exchange channels at a temperature of about 20° C. The flowing film contacting zone has a vertical length of about 2 meters.

We claim:

1. A process for the reaction of a thin film liquid stream with a gaseous reactant, said process comprising:
  - passing a first stream comprising a liquid as a plurality of thin films down a plurality of corrugated surfaces defined by a plurality of vertical plates;
  - maintaining sufficient space between said plates to avoid direct contact between adjacent films;
  - passing a gaseous phase reactant stream through open vertical channels defined by said vertical plates into contact with the thin film; and,
  - recovering a reaction product from said plates.
2. The process of claim 1 wherein the reaction is the sulfonation of a substrate with sulfur trioxide.
3. The process of claim 1 wherein a heat exchange fluid contacts one side of each plate to indirectly transfer heat with the film.
4. The process of claim 1 wherein said corrugations run at least partially transverse to the flow of said falling film.
5. The process of claim 4 wherein said corrugations extend diagonally across the surface of the plates in a plurality of rows and the vertical length of each diagonal is less than the vertical height of the plates.
6. The process of claim 4 wherein the corrugations run horizontally.
7. The process of claim 6 wherein a heat exchange plate is positioned between the vertical plates to define heat exchange channels for a heat exchange fluid and the heat exchange plates define corrugations that are transverse to the horizontal corrugations.
8. The process of claim 1 wherein said gaseous stream passes downwardly through said channels.
9. The process of claim 1 wherein either the amplitude or the frequency of the corrugations is established to induce a desired degree of turbulence into said liquid as it passes down said corrugated surface.
10. A process for the sulfonation of fluid organic substances, said process comprising:
  - passing a first stream comprising an organic liquid as a plurality of thin films down a plurality of corrugated surfaces defined by a plurality of vertical plates;
  - maintaining sufficient space between said plates to avoid direct contact between adjacent films;
  - passing a gaseous phase stream containing SO<sub>3</sub> through open vertical channels defined by said vertical plates into contact with the thin film; and,
  - recovering an effluent from said plates containing a sulfonated reaction product.
11. A process for the ethoxylation of fluid organic substances, said process comprising:
  - passing a first stream comprising an organic liquid comprising an ethoxylation substrate as a plurality of thin films down a plurality of corrugated surfaces defined by a plurality of vertical plates;
  - maintaining sufficient space between said plates to avoid direct contact between adjacent films;
  - passing a gaseous phase stream containing ethylene oxide through open vertical channels defined by said vertical plates into contact with the thin film; and,
  - recovering an effluent from said plates containing an ethoxylated reaction product.
12. The process of claim 11 wherein said ethoxylation reactant comprises an alcohol or an alkylphenol.

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# United States Patent

Asher et al.

[19]

[11]

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[45]

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## PROCESS WITH POROUS MEANS TO CONTROL REACTION RATE AND HEAT

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[73] Assignee: SRI International, Menlo Park, Calif.

[\*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: 08/761,598

[22] Filed: Dec. 6, 1996

### Related U.S. Application Data

[63] Continuation of application No. 08/205,183, Mar. 2, 1994, Pat. No. 5,583,240, which is a continuation-in-part of application No. 08/024,989, Mar. 2, 1993, abandoned.

[51] Int. Cl. C07C 53/00

[52] U.S. Cl. 554/98; 562/74; 562/95; 562/109; 562/110; 562/123; 568/601

[58] Field of Search 554/98; 562/74; 562/95, 109, 110, 123; 568/601; 585/276; 423/659; 422/135, 238, 239

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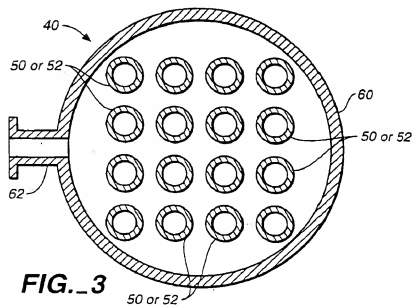
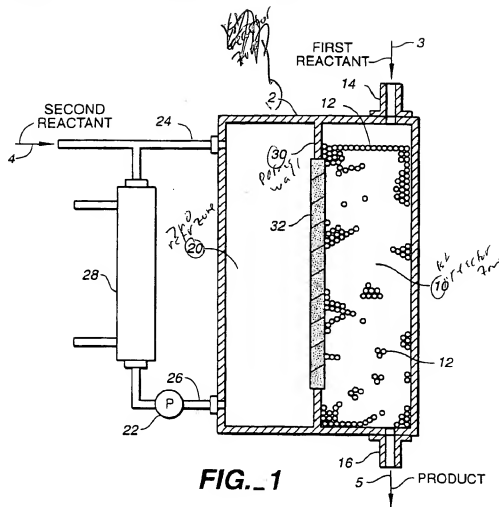
Attorney, Agent, or Firm—Peters, Verny, Jones & Bksa, LLP

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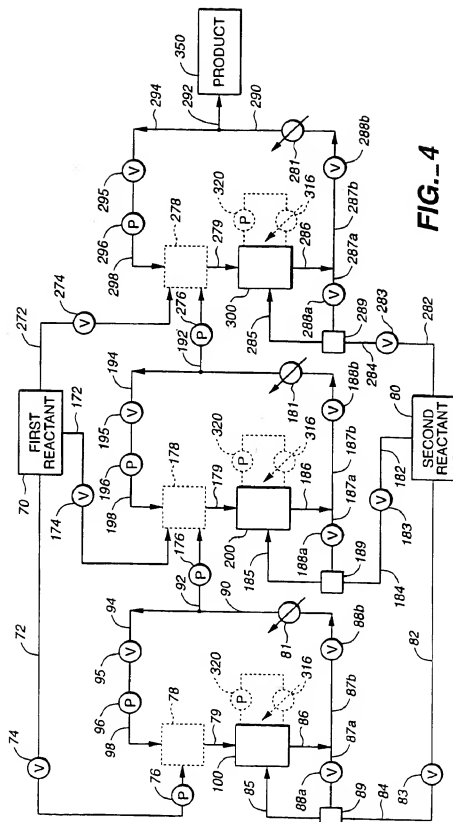
### ABSTRACT

An process for forming a product which may be in a liquid phase is disclosed wherein a first reactant, preferably a liquid reactant, is directly fed into a reaction zone containing mixing elements and which comprises a first compartment of a reactor. A second reactant, which is maintained at a higher pressure, is fed into a second compartment of the reactor separated from the first compartment by a porous wall. The second reactant passes through this porous wall into the reaction zone to react with the first reactant. The process thereby controls rates of the reactions and the exothermic heats generated by the reactions. Pulsatile flow in one or both reaction compartments improves mixing. An evaporator for a portion of the product improves product quality and permits higher reaction temperatures in the reactor.

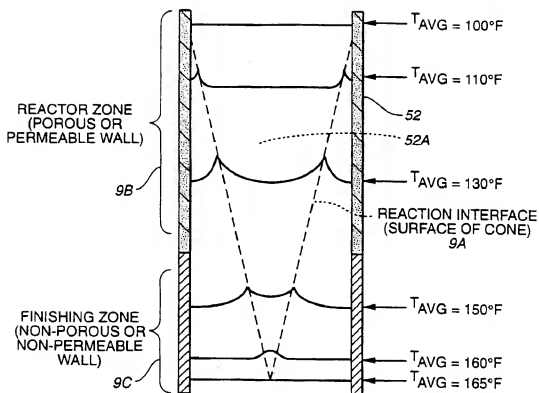
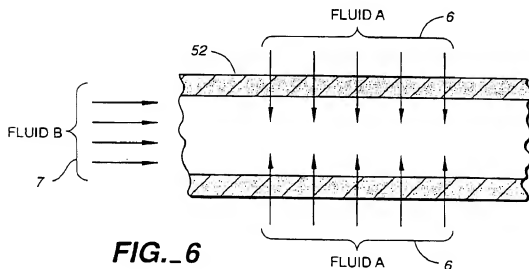
39 Claims, 6 Drawing Sheets

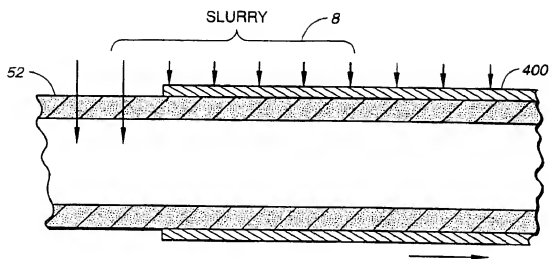
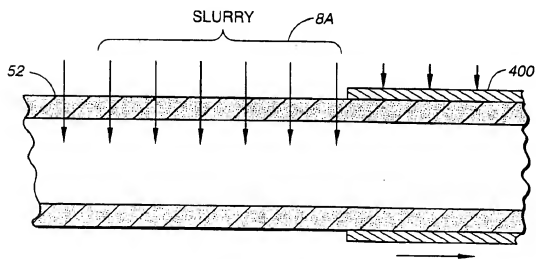




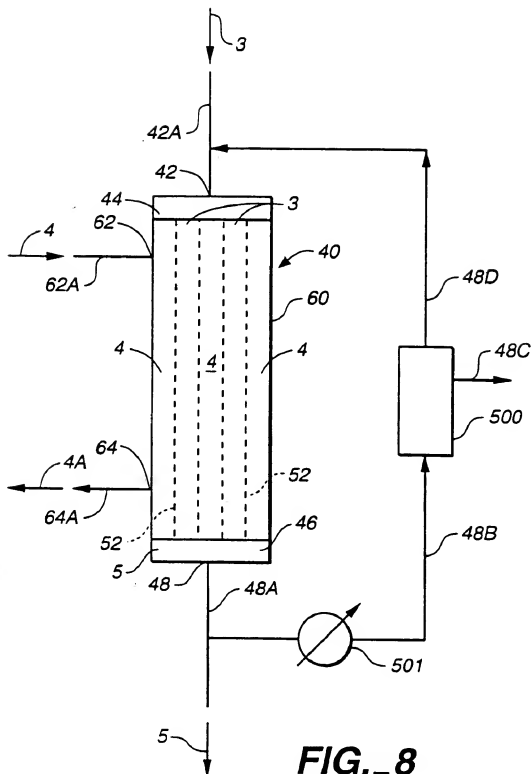


**FIG. 4**

**FIG.\_5****FIG.\_6**

**FIG.\_7A****FIG.\_7B**





# PROCESS WITH POROUS MEANS TO CONTROL REACTION RATE AND HEAT

## RELATED APPLICATIONS

This is a continuation of application, Ser. No. 08/205,183, filed on Mar. 2, 1994 now U.S. Pat. No. 5,583,240, which is a continuation-in-part of abandoned application Ser. No. 08/024,989 filed Mar. 2, 1993. This prior application is incorporated herein by reference in its entirety.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to a controlled process for reacting together two or more reactants. One reactant is fed at a first pressure into a first zone in a reactor containing mixing means and a second reactant is fed at a higher pressure into a second zone in the reactor. The second zone is separated from the first zone by a porous barrier wall through which the second reactant passes. In this way, a controlled flow of second reactant into the first reactor zone and control of the reaction are achieved.

### 2. Description of The Related Art

Processes for forming a reaction product from at least two reactants wherein the desired product is a liquid phase or high density supercritical phase at the reaction conditions are typically carried out in a thin film reactor such as a falling film reactor. For example, Ashina et al. in U.S. Pat. No. 3,918,917 describes a multi-tube thin-film type reaction apparatus for the reaction of an organic compound and gaseous sulfur trioxide comprising a reaction tube provided with gas and liquid feeding tubes at the upper end of the reaction tube.

It is also known to carry out such reactions radially by passing reactants into a cylindrical reactor through the outer walls of the cylinder and to collect the resultant product through an apertured central tube in the cylindrical reactor.

For example, Newson in U.S. Pat. No. 3,844,936 discloses a radial desulfurization process and apparatus wherein both oil and hydrogen are peripherally introduced through sidewall nozzles into a cylindrical shell packed with catalyst. A tube having apertures therein passes through the center of the cylindrical shell, and both the oil and the hydrogen gas, passing through the catalyst in the outer shell, enter the central tube through the apertures and leave the apparatus.

De Rosset in U.S. Pat. No. 3,375,288 discloses a process and apparatus for dehydrogenation of hydrocarbons wherein a hydrocarbon feedstock to be dehydrogenated is fed into a reaction zone containing a particulate dehydrogenation catalyst. The reaction mixture, while undergoing dehydrogenation, is also contacted with one side of a tubular thin permeable membrane, such as a silver tube which has a high permeability to oxygen. Oxygen at a higher partial pressure is maintained on the opposite surface of the tube and diffuses through the tube to react with the hydrogen being liberated in the dehydrogenation process.

The use of permeable membrane catalysts, particularly the use of palladium alloy catalyst membranes, have been the subject of much investigation. Mischenko et al. in U.S. Pat. No. 4,179,470 describe a process for producing aniline by catalytic hydrogenation of nitrobenzene which comprises using a membrane catalyst which is essentially an alloy of palladium and ruthenium. The hydrogenation is carried out by feeding nitrobenzene on one side of the membrane catalyst and hydrogen on the other side. The hydrogen

reactant diffuses through the membrane catalyst, which is shaped as a foil, into the hydrogenation chamber containing the nitrobenzene reactant.

Gryaznov et al., in an article entitled "Selectivity in Catalysis by Hydrogen-porous Membranes", published in Discussions of the Faraday Society, No. 72 (1982) at pages 73-78, disclose the use of hydrogen-porous membrane catalysts through which hydrogen may pass, either during a dehydrogenation reaction to raise the reaction rate and/or suppress side reactions; or during a hydrogenation reaction to independently control to some extent the surface concentration of hydrogen and to obtain incompletely hydrogenated products which are thermodynamically unstable in the presence of hydrogen.

V. M. Gryaznov, in an article entitled "Hydrogen Permeable Palladium Membrane Catalysts", published in Platinum Metals Review, 1986, 30, (2) at pages 68-72, describes the catalytic properties of selected palladium binary alloy membranes, which are only permeable to hydrogen, during hydrogenation and dehydrogenation reactions.

Armor, in a review entitled "Catalysis with Permselective Inorganic Membranes", published in Applied Catalysis, 49 (1989) at pages 1-25, discusses the work of others with various catalytic membranes, including hydrogen-permeable palladium membranes, ceramic-supported palladium membrane catalysts, ceramic membranes permeable to oxygen, porous polymer resins used as membranes catalysts, and alumina membrane catalysts.

K. Omata, et al., in *Applied Catalysis*, Vol. 52, L1-L14 (1989) disclose the oxidative coupling of methane using a membrane reactor. The catalyst is on the membrane or barrier, and the reactor has no mixing elements.

W. M. Haunschild in U.S. Pat. No. 4,624,748 discloses a catalyst system for use in a distillation column reaction. The entire reaction mixture passes through the permeable material. These ether-forming reactions occur at low temperatures up to about 100° C. Higher temperatures apparently would destroy the membrane.

All patent applications, patents, articles, references, standards and the like cited herein are incorporated herein by reference in their entirety.

What is needed is a process that makes it possible to control the rate of a chemical reaction by controlling the rate of contact of the one or more reactants. The present invention accomplishes these objectives of controlling reaction rate by using a porous barrier through which one or more of the reactants is introduced to the zone containing the other reactant(s), and contacting them using mixing elements.

## SUMMARY OF THE INVENTION

The present invention comprises a process for forming a product which may be in a liquid phase wherein a first reactant, or combination of first reactants, is directly fed into a reaction zone containing mixing elements and a second reactant or a combination of second reactants, which is maintained at a higher pressure, is transported through a porous barrier into the reaction zone to react with the first reactant. Preferably, the first reactant is a liquid and the second reactant is also a liquid. Control of both the reaction rate and control of the exothermic heat are made possible by the process.

In one embodiment, the present invention relates to an improved process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

(a) feeding into a first reactor zone one or more first reactants at a first pressure;

(b) feeding one or more of the second reactants at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the second reactant; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone; whereby one or more second reactants will pass through the porous wall to contact one or more first reactants in the first reactor zone and form the product.

In another embodiment, the present invention relates to an improved process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

(a) feeding into a first reactor zone containing mixing elements therein one or more first reactants at a first pressure;

(b) feeding one or more second reactants at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the one or more second reactants; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby one or more second reactants will pass through the porous wall to contact one or more first reactants in the first reactor zone and form the product.

In another embodiment, the present invention relates to an improved exothermic process for forming a product by reaction of one or more first liquid reactants with one or more second liquid reactants which comprises:

(a) feeding one or more first liquid reactants at a first pressure through a first reactor zone having mixing elements therein;

(b) feeding one or more second liquid reactants at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by one or more second liquid reactants; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby one or more second liquid reactants will pass through the porous wall to contact one or more first liquid reactants in the first reactor zone and form the product.

In yet another embodiment, the present invention relates to an improved exothermic process for forming a product by reaction of one or more liquid first reactants with one or more second reactants, at least one of which is gaseous at ambient conditions, which comprises:

(a) feeding one or more liquid first reactants at a first pressure through a first reactor zone having mixing elements therein;

(b) feeding one or more second reactants, at least one of which is gaseous at ambient conditions, at a second pressure

higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the one or more second reactants; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby the one or more second reactants passes through the porous wall to contact the one or more liquid first reactants in the first reactor zone and form the product.

In still another embodiment, the present invention relates to an improved exothermic process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

(a) feeding a first reactant at a first pressure through a first reactor zone containing mixing elements having at least one dimension equal to from about  $\frac{1}{4}$  to about  $\frac{1}{100}$  of the largest dimension of the first reactor zone normal to the flow of the first reactant through the first reactor zone;

(b) feeding a second reactant at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the second reactant; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby the second reactant passes through the porous wall to contact the first reactant in the first reactor zone and form the product.

In still another embodiment, the present invention relates to an improved process for forming a product by reaction of a first liquid reactant with a second liquid reactant, which process comprises:

(a) feeding a first liquid reactant at a first pressure into a first reactor zone containing particles having at least one dimension equal to from about  $\frac{1}{4}$  to about  $\frac{1}{100}$  of the largest dimension of the first reactor zone normal to the flow of the liquid reactant through the first reactor zone;

(b) feeding a second liquid reactant at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the second liquid reactant; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby the second liquid reactant passes through the porous wall to contact the first liquid reactant in the first reactor zone and form the product.

In still another embodiment, the present invention relates to an apparatus for forming a product by reaction of one or more first reactants with one or more second reactants, which apparatus comprises:

a reactor having one or more porous members therein dividing the reactor into first and second reactor zones capable of being maintained at different pressures; whereby the one or more first reactants in the reactor zone maintained at a higher pressure will pass through the one or more porous

members into the reactor zone maintained at a lower pressure to contact one or more second reactants in the reactor zone maintained at a lower pressure to form the product.

In still another embodiment, the present invention relates to any of the improved processes described herein, wherein the process further includes step (d), (e) and (f);

(d) conveying a portion of the reaction product of step (c) to an evaporator;

(e) separating volatile reactants or reaction products wherein the vapor pressure of the volatile reactants or reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c); and

(f) optionally recycling all or a portion of all of the reaction product liquid now depleted of volatile reactants, reaction products or a combination thereof to the first reactor zone of step (a).

In another aspect, the rates of flow of the first reactant in the reactor are cyclic (pulsatile) from a maximum flow rate in one direction to a rate of about a 20% reverse flow of the maximum flow rate, and return to maximum flow rate.

In another aspect, the present invention also concerns a separation, e.g. a flash evaporation, of reactants or reaction products. This separation improves the yield of the final product by reducing unwanted side reactions and reduces the formation of unwanted by-products.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a partially cutaway vertical cross-sectional view illustrating the process of the invention being carried out in its simplest form.

FIG. 2 is a schematic representation of a vertical cross-sectional diagrammatic view of an apparatus suitable for use in carrying out the process of the invention.

FIG. 3 is a top view, in cross-section of the apparatus of FIG. 2 taken along lines 3—3.

FIG. 4 is a schematic representation of a diagrammatic view of a series of stages of the apparatus generally illustrated in FIGS. 2 and 3.

FIG. 5 is a schematic representation of a graph depicting the temperature and a conical reaction interface along the flow line within a tubular reactor. Those skilled in the art will recognize that dependent on relative reaction rates and transport rates, the reaction interface can assume many different shapes.

FIG. 6 is a schematic representation of a diagrammatic illustration of the respective flows of Fluid A across the walls of the porous tube and Fluid B through the tube.

FIG. 7A is a schematic representation of a cross-sectional view illustrating how the porosity of a porous tube may be varied along its length, with a shield over a portion of the porous tube.

FIG. 7B is a schematic representation of a cross-sectional view illustrating how the porosity of a porous tube may be varied along its length, with the shield shown in FIG. 7A moved to expose a further portion of the porous tube.

FIG. 8 is a schematic representation of the apparatus of the process additionally having the separator (or evaporator) component and recycle mode.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises an process for forming a chemical product which may be in a liquid phase wherein a first reactant, preferably a liquid reactant, is directly fed into a reaction zone containing mixing elements and which

comprises a first compartment of a reactor. A second reactant which may be either a liquid or gaseous reactant, and which is maintained at a higher pressure, is fed into a second compartment of the reactor separated from the first compartment by a porous wall or barrier. The second reactant passes through this porous wall into the reaction zone containing mixing elements to react with the first reactant under controlled reaction conditions.

Basic Apparatus Useful in the Process

Referring now to FIG. 1, the concept of the process of the invention is illustrated in its simplest form. Within a reactor 2, a first reactor compartment or zone 10 and a second reactor compartment or zone 20 are provided, separated by a wall 30 having a porous portion 32 spaced from both the top and bottom of wall 30. Reactor zone 10 is packed with mixing elements 12, such as glass balls, preferably to a level above porous portion 32 of wall 30 so as to introduce mixing into the first reactant stream 3 prior to transporting the second reactant into reactor zone 10.

A first reactant 3, which is preferably in a liquid phase, is fed through an entrance port 14 into first reactor zone 10 and a second reactant 4, which is at a higher pressure than the pressure in first reactor zone 10, is fed through entrance port 24 into second reactor zone 20. The second reactant 4 passes through porous wall portion 32 into first reactor zone 10 where it reacts to form a product 5 which is removed from first reactor zone 10 via exit port 16.

If desired, an exit port 26 is provided in second reactor compartment 20 to permit the second reactant 4 to be circulated through second reactor compartment 20, using a pump 22. As shown in FIG. 1, a heat exchanger 28 may be optionally used to cool the circulating second reactant to control the heat in reactor 2.

In a preferred mode, as shown in FIGS. 2 and 3, the reaction will be carried out in a multiple tube reactor 40 having one or more tubes 50 housed in an outer shell 60 wherein a portion 52 of the wall of each tube 50 will comprise porous material. Mixing elements 58 are placed within each tube 50 and a first reactant 3, which preferably is a liquid reactant, will be fed through an inlet port 42 in the top of reactor 40 into an inlet plenum or manifold 44 connected to the open end 54 of each tube 50. It will be noted that preferably mixing elements 58 are also placed in inlet manifold 44 so that mixing flow conditions are already created in the flow of first reactant in reactor 40 before the first reactant reaches tubes 50 and, therefore, before introduction of the second reactant 4 into the flow stream.

While 16 such tubes are illustrated in the reactor shown in FIGS. 2 and 3, it will be understood that this is for illustrative purposes only and a commercial embodiment for practicing the process of the invention would utilize a large number of such tubes, e.g., as many as 50 or more such porous tubes.

The second reactant 4 is introduced through a first side port 62 in shell 60 of reactor 40 at a higher pressure than the first reactant to circulate around all of the outside surfaces of tubes 50, including the porous portions 52 through which the second reactant is transported to contact and react with the first reactant 3 within tubes 50.

The resultant product 5, as well as any unreacted reactants, may then exit via open bottom ends 56 of each tube 50 into a second plenum or manifold 46 which, it will be noted, also contains mixing elements 58. This positioning of mixing elements 58 along the entire length of each tube 50, even beyond the porous portion of each tube 50 and into lower manifold 46, is provided because there may be continued reaction between the first reactant 3 and second

reactant 4 even after the flow of product 5 and reactants (3 and 4) passes beyond the porous portion of each tube 50. That is, the reaction zone may extend beyond the end of the porous portion of each tube 50.

The product 5, as well as any unreacted reactants, may leave reactor 40 via exit port 48 at the bottom of reactor 40. An exit port 64 in shell 60 of reactor 40 is also provided for the second reactant 4 to permit circulation thereof, as well as possible additional use of the second reactant as a coolant for reactor 40, as discussed above.

FIG. 5 is a schematic representation of a graph which depicts the change in temperature and a conical reaction interface 9A along the flow line within a porous tubular reactor, e.g. 52, having a reactor zone 9B. Within tube 52 is found a radial reaction zone 52A surrounded by a porous wall through which the second reactant 4 passes to react with the first reactant 3. The finishing zone 9C is not porous. The average temperatures are shown at various points in the tube. The graph illustrates that the temperature within the reactor gradually rises with no hot spots in the reactor, e.g. 40.

The porous barrier 52 may or may not have catalytic properties. Preferably the barrier or wall does not have catalytic properties.

#### Mixing Elements Used in Process

The presence of mixing elements 58 in the reaction zone provide a more thorough mixing of the reactants in the reaction zone to prevent or inhibit the occurrence of hot spots in the reaction zone which could result in creation or concentration of excessive heat which could damage either reactants or product. Other applicable mixing elements have been patented and used commercially. These include those that were covered by U.S. Pat. Nos. 3,922,220 and 3,862,022 and are commonly identified as Kenics static mixers in the patent and scientific literature and available from Kenics Corporation, 125 Flagship Drive, North Andover, Mass. 01845. The mixing elements preferably comprise inert materials such as glass or ceramic balls or other non-reactive packing type material such as Raschig rings or beryl saddles. In some embodiments, the mixing elements are stationary. In other embodiments, the mixing elements are mobile within the reaction zone. In one embodiment, the mixing elements do not have catalytic properties.

It is also within the scope of the invention, in another embodiment, for the mixing elements to have catalytic properties as well, although it will be appreciated that the main purpose of the mixing elements is to create multiple divisions and recombining of flow and thus provide for more thorough mixing of the reactants in the reaction zone in the reactor.

Thus, particulate catalysts conventionally utilized usually comprise finely divided materials characterized by high surface areas and short diffusion distances to maximize the contact area between catalyst and reactants, at the expense of high pressure drops, resulting in lower throughput or the need to utilize more energy in passing the reactants through such a catalyst bed.

In contrast, the mixing elements utilized in the process of the invention are much larger in size than conventional catalysts so that any negative impact on flow rates by the presence of such mixing elements will not be significant.

Preferably the mixing elements utilized in the process of the invention have a major dimension which ranges from about  $\frac{1}{16}$  to about  $\frac{1}{2}$ , preferably from about  $\frac{1}{16}$  to about  $\frac{1}{2}$ , of the largest dimension in the plane of the reaction zone normal to the flow of the reactants through the reaction zone. For example, when the mixing elements are commonly known Kenics elements in a cylindrical tube, the elements

bisect the tube diameter and function as mixing elements because they are bisected by the elements upstream into two functional elements. Thus, the characteristic major dimension in this example is  $\frac{1}{2}$  of the diameter of the tube. For example, when the mixing elements comprise balls and the reaction zone comprises a cylindrical tube, the balls will have a diameter of from about  $\frac{1}{16}$  to about  $\frac{1}{2}$ , preferably from about  $\frac{1}{16}$  to about  $\frac{1}{2}$ , of the diameter of the tube. Thus, if the reaction zones are located within 2 cm cross sectional inner diameter (I.D.) tubes having porous tube walls, spherical mixing elements utilized within the tubes will have diameters ranging from about 0.2 millimeters (mm) to 10 mm, and preferably will range from about 2 mm to 6.7 mm.

It should be further noted that while the presence of the mixing elements has been illustrated in the reaction zone, as well as in the region just prior to the mixing zone, the mixing elements may also be reset in the conduits leading from the reactor to heat exchangers, and may even be used in the heat exchanger tubes as well. This is particularly true where the reaction zone, comprising the porous portion of a tube and the region of the tube beyond the porous region, is joined to a heat exchanger forming an extension of the same tube, in which case the entire tube is advantageously packed with such mixing elements.

The above configuration makes maximum uses of the tube volume. However, for many chemistries, the concern about the effects of possible leakage between the shell side fluids, the second reactant, and the cooling water would preclude its use. For example, in the case of sulfonating an organic compound, the second reactant 4 is  $\text{SO}_3$ , which would be separated from the cooling water by a tube sheet. A pin hole would produce hot sulfuric acid which would soon enlarge the pin hole. In these cases, separate reactors and heat exchangers would be preferred.

#### Porous Material Used in the Process

The porous material initially separating the two reactants, and through which the second reactant passes, will generally comprise a material of controlled porosity, as opposed to a pore-free permeable membrane through which transport is by diffusion, since such pore-free membranes provide poor rate performance due to the low transport rate across the membrane. The porosity and pressure are adjusted to provide a minimum flow of the second reactant across the porous material, relative to the flow of the first reactant on the low pressure side of the porous material (32 and/or 52), sufficient to permit reaction of the first reactant on the low pressure side with the second reactant passing through the porous material.

However, the flow rate of the second reactant 4 across the porous material, i.e., the porosity and pressure used, must be adjusted to not exceed that flow rate which will provide either reaction between the reactants or dissolving of the second reactant 4 into the first reactant 3 on the low pressure side, i.e., a second phase (comprising the high pressure second reactant) should not be substantially formed in the reaction zone. By "substantially" is meant that not more than 10% of the high pressure second reactant passing through the porous material (32 and/or 52) should form a second phase in the reaction zone.

Typically, the porous material will comprise a sintered metal. The porous material may comprise a high porosity (coarse) material which has been coated with a second material to control the pore size. For example, a porous stainless steel material may be coated with a non-reactive ceramic material such as zirconia. This, for example, could be done by coating a commercially produced sintered stainless steel tube with finely divided zirconia or titania powder

dispersed in a vehicle, allowing the vehicle to evaporate, and then firing the zirconia (or titania)-coated tube at a temperature of 1000° C.

The coating of the commercially produced porous tube may be carried out by pumping a slurry or suspension of the coating materials, e.g., zirconia or titania, through the walls of the porous tube, i.e., from the outside of the tube to the inside—or vice versa—until one achieved the desired porosity. When the coating or changing of the porosity is done by pumping a slurry from the outside to the inside of the porous tube, the need for heating to stabilize the porosity of the tube can sometimes be eliminated.

In an embodiment of such modification of an existing porosity of porous tube 52, it may be advantageous to provide a variable or profiled porosity in porous tube 52. Referring to the graph of FIG. 6, the pressure of Fluid B (aka 7) traveling inside porous tube 50 gradually drops as Fluid B (7) flows within tube 52. This, in turn, means that the change in pressure  $\Delta P$ , across the porous wall of tube 52 increases along the tube in the direction of flow of Fluid B (7) (assuming that Fluid A (aka 6) has a constant pressure all along the length of tube 50 and/or 52).

To compensate for this variable pressure drop across the wall of tube 52, there should be a continually decreasing porosity in the porous wall of tube 52. One way of achieving this, as shown in FIGS. 7A and 7B, is to cover either the inside or outside surface of porous tube 52 with a sleeve 400 which is slowly moved or retracted as the slurry 8 or suspension of the coating materials, e.g., zirconia or titania, is pumped through the walls of the porous tube. By varying the amount of material pumped through the porous walls of the tube along the length of the tube in this manner, a profiled change in the porosity of the tube may be achieved, with the portion of the tube 8A exposed the longest to the coating materials having the lowest porosity and, therefore, being located on the downstream end of the flow of Fluid B (or 7) through the tube.

The porosity of a porous metal substrate, such as a commercially available porous stainless steel tube, could also be modified by coating the porous tube with fine metal particles, and then sintering the coated tube at a temperature sufficiently low to permit the particles to sinter to the porous substrate without fusing the porous substrate into a non-porous mass. Examples of metal powders which may be used, for example, with a porous stainless steel tube include stainless steel, nickel, and chromium.

The porosity of the porous surface separating the first 3 and second reactants 4 will be selected to provide a volumetric flow rate of second reactant through the porous barrier which will result in the desired rate of reaction between the reactants. If the exothermic heat given off during the reaction is high, in accordance with the process of the invention, the reaction may be slowed by lowering the flow of the second reactant into the reaction zone. This may be accomplished, in accordance with the present invention, by selecting a barrier material having a lower porosity.

The viscosity of the reactant which is flowing through the porous barrier, as well as the pressure difference between the two sides of the porous barrier and the area of the porous barrier, also must be taken into account when attempting to adjust the volumetric flow of the second reactant across the porous barrier to thereby exercise control of the generation of exothermic heat in the reaction zone. This viscosity, if desired, may be further controlled or adjusted by blending product with the particular reactant before feeding the reactant into the reaction zone.

When these parameters are all taken into account, the porosity of a porous barrier of given area to a reactant of

given viscosity at a given pressure differential across the barrier to achieve a particular volumetric flow rate may be expressed in the following equation:

$$V = \frac{Q \cdot A \cdot \Delta P}{\mu}$$

wherein:

V= volumetric flow rate of the reactant going through the porous barrier, in cubic centimeters per second (cc/sec);  
A= the outside area of the porous barrier in square centimeters (cm<sup>2</sup>);

$\mu$ = the viscosity of the second reactant passing through the porous barrier in centipoise (cp);

$\Delta P$ = the change or difference in pressure from one side of the porous barrier to the other side in pounds per square inch (psi); and

Q= the viscosity normalized permeability of the porous barrier material in cm<sup>3</sup> cp/cm<sup>2</sup> sec psi (where 1 pound per square inch (psi) is equal to 6894.7 pascal).

It will, of course, be recognized that this "viscosity normalized permeability" of a given material will vary with the porosity of the material, the wall thickness of the porous barrier, and the wall morphology, since the porosity may not be uniform. In accordance with the invention, the Q value of the porous barrier initially used to separate the first and second reactants should range from about 10<sup>-6</sup> to about 5x10<sup>-2</sup> cm<sup>3</sup> cp/cm<sup>2</sup> sec psi, preferably from about 10<sup>-6</sup> to about 10<sup>-4</sup> cm<sup>3</sup> cp/cm<sup>2</sup> sec psi, and most preferably from about 5x10<sup>-6</sup> to about 5x10<sup>-5</sup> cm<sup>3</sup> cp/cm<sup>2</sup> sec psi, to provide the desired initial separation while still permitting adequate permeance of the second reactant through the barrier to permit the reaction to proceed. The mean pore diameter of the pores in the barrier, depending upon its application, may generally range from between about 0.01 and 50 micrometer.

The temperature range maintained in the reactor 40 may range from the lowest temperature at which the particular second reactant 4 will still pass through the porous material, and at which both reactants (3 and 4) will be in either the gaseous or liquid states, i.e., will not become solidified. Apart from this, the low end of the temperature range maintained within the reactor will usually depend upon the desired process economics since some reactions will be unacceptably slow if the temperature is maintained too low.

The upper end of the temperature range maintained within the reactor will usually be from about 5° C. to about 200° C. below that temperature at which significant product degradation or undesirable side product formation occurs. By "significant" is meant 10% or more of the product degrades or 10% or more of the reaction product comprises the product of a side reaction.

Usually the temperature within the reactor will be within a range of from about -50° C. to about 500° C. (depending upon the particular reactants), preferably from about 0° C. to about 400° C. (again depending upon the particular reactants) and more preferably between about 110° and 400° C. (depending upon the particular reactants). For example, the reactor will be maintained within a range of from about 100° C. to about 200° C. for an ethoxylation reaction, while for a typical sulfonation process, the reactor temperature maintained within a range of from about -20° C. to about +100° C.

The outlet pressure of the reactor may be maintained at any conventional pressure used in state of the art reactors consistent with the minimum pressure needed to obtain

sufficient desired product flow up to the maximum pressure which may be handled by downstream equipment, e.g., a high pressure needed to couple with downstream processing.

Inlet pressures of the reactants must be consistent with the desired outlet pressure and the pressure drop within the reactor. The differential in inlet pressure between the first and second reactants will be a function of the permeability of the second reactant—which will, in turn, be dependent upon the physical properties of the second reactant and the porosity of the porous material in the apparatus.

It should be noted that the pressure within the second reaction zone at all locations of the porous wall should be maintained higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone.

#### Reactions and Reactants Used in the Process

There are many reactions which benefit from the application of this invention. By way of examples of reactions which may be carried out using the process and apparatus of the invention, and not by way of limitation, there may be mentioned oxidations, halogenations, sulfonations, sulfations, nitrations, ethoxylations, hydrogenations, polymerizations and the like. State of the art conditions for these reactions, therefore, extend over very broad ranges of temperature and pressure.

To practice the present invention with these conditions, one of skill in the art should select the conditions for the reaction first zone to be quite near those conditions used with state of the art reactors for the reactions considered. The advantage of using the present invention is less local temperature excursions within the reactor, and better control of the transport of reactants and products throughout the reaction zone and process yielding higher quality, and more uniform reaction products.

The respective flow rates of the reactants into the reactor will, of course, depend upon a number of parameters including those just discussed, as well as the overall size of the reactor. The relative rates of reactant flow, i.e., with respect to one another, will depend upon the particular reaction, including the amount of heat generated, as well as whether or not the process will be carried out in one or more stages.

It may be desirable, when the process is conducted in a single stage apparatus, to circulate some of the product stream back to the inlet side of either or both reactants in some instances to thereby provide a further control of the reaction rate or to alter the viscosity of one of the incoming reactant flows. In the case of the first reactant 3, such dilution will result in less reactant present per given mass and heat capacity of this total flow going into the zone 1 of the reactor. Thus, the total exothermic heat of the reactions of all of this first reactant mixture 3 will result in a lower final temperature because of the larger heat capacity. Addition of the product to the second reactant stream 4 will (in many cases) serve to increase the viscosity of the second reactant stream passing through the porous barrier, thus decreasing the volumetric flow rate of second reactant passing through the porous barrier (in accordance with the previous equation) which will also serve to slow down the reaction and reduce the generation of exothermic heat.

#### Multiple Stage Apparatus for Conducting the Process

The preferred mode of operating the process of the invention will be in a plurality of stages, using, for example, in each stage, a shell and tube reactor such as previously described and illustrated in FIGS. 2 and 3, together with optional recirculation of product, optional addition of makeup reactants, and optional use of heat exchangers to control the overall temperature buildup as needed.

Such apparatus is illustrated in block diagram form in FIG. 4 which illustrates three stages of operation of the process of the invention. The first reactant from source 70 travels via conduit 72 through valve 74 and pump 76 to an optional mixer 78 where the first reactant stream 3 may be optionally blended with a portion of the product stream from first reactor 100. The first reactant 3 then travels via conduit 79 into first reactor 100, which may be a shell and tube reactor similar to reactor 40 previously depicted in FIGS. 2 and 3. In this case, conduit 79 would be connected to inlet manifold 44 (FIG. 2) within reactor 100 so that the first reactant 3 flows through the tubes containing mixing elements within reactor 100 connected to inlet manifold 44.

The second reactant 4, from second reactant source 80, passes via conduit 82 through valve 83 and then through conduit 84 to optional blender 89 and then through conduit 85 to enter the shell portion of first reactor 100. As previously described with respect to FIGS. 2 and 3, the second reactant 4 then passes from the shell through the porous portions of the tubes within reactor 100 to react with the first reactant 3 flowing through the tubes.

The resulting product 5, as well as any unreacted reactant (s), leave first reactor 100 via conduit 86, where the product stream splits into two streams. Conduit 87a optionally returns some of the product stream through valve 88a to optional blender 89 where it is blended with the second reactant stream and is then fed via conduit 85 into reactor 100. The remainder of the product stream passes through conduit 87b to valve 88b and then through heat exchanger 81 and conduit 90. Conduit 90 then also splits into two portions. Conduit 92 passes a portion of the product stream to the next stage, and conduit 94 through which one may optionally recirculate product 5 back to reactor 100.

The portion of the product stream optionally recycled back to reactor 100 through conduit 94 passes through a valve 95 (which controls the ratio of product stream being recycled back to reactor 100) to pump 96 which is connected to mixer 78 via conduit 98.

By shutting off both valves 88a and 95, all of the product stream will be passed on to the subsequent stage of the apparatus. Shutting off only one of valves 88a or 95 will respectively recycle the product stream back to only one of the initial reactant streams as desired.

Similarly, the relative flows of the first and second reactants into reactor 100 may be controlled by adjustment of valves 74 and 83, as well as valve 88b, either by itself (when valve 88a is shut off) or in conjunction with valve 88a, to control the flow rate through reactor 100.

The portion of the product stream to be passed on to the next stage via line 92 passes through pump 176 to optional mixer 178 where it is optionally blended with recycled product from the second stage as well as with an optional flow of further first reactant from first reactant source 70 via line 172 and valve 174, which controls the amount of fresh first reactant to be blended with the product stream from reactor 100.

The product stream from reactor 100, with or without further amounts of fresh first reactant and recycled product from the second stage, is fed into second reactor 200 via line 179. As previously described with respect to reactor 100, second reactor 200 would preferably be constructed similarly to reactor 40 illustrated in FIGS. 2 and 3, so the incoming stream from line 179 would pass into the interior of the porous tubes of the reactor via the inlet manifold.

Optional additional second reactant would then flow, via line 182 and valve 183 from second reactant source 80 to an optional blender 189 from which it would flow via conduit 185 to the shell side of reactor 200.

The product stream, emerging from reactor 200 via conduit 186, is split into two streams (as in the first stage). One stream which will flow via conduit 187a through valve 188a to optional blender 189 where it can be blended with fresh second reactant. The other stream will flow via conduit 187b to valve 188b and heat exchanger 181. The stream then flows via conduit 190 to a point where it again may be split between two streams to either pass on to the third stage via conduit 192 or to recirculate via conduit 194 and valve 195 back through pump 196 and conduit 198 to optional blender 178 where the product stream may be blended with fresh first reactant 3.

Similarly, in the third stage, the product stream in conduit 192 may be pumped through pump 276 to optional blender 278 where it may be optionally blended with fresh first reactant 3 entering blender 278 from source 70 via conduit 272 and valve 274, as well as with recycled product from reactor 300, as will be described below, before entering reactor 300 via conduit 279. Reactor 300 is also preferably be constructed in accordance with the previously described construction with respect to FIGS. 2 and 3. Thus, the incoming stream via conduit 279 enters the inlet manifold to be distributed to the porous tubes within reactor 300.

Optional additional second reactant 4 would then flow, via line 282 and valve 283 from second reactant source 80 to optional blender 289 from which it would flow via conduit 285 to the shell side of reactor 300.

The product stream, emerging from reactor 300 via conduit 286, is then split into two streams (as in the first and second stages). One stream which will flow via conduit 287a through valve 288a to optional blender 289 where it can be blended with fresh second reactant 4. The other stream will flow via conduit 287b to valve 288b and heat exchanger 281. It then flows by way of conduit 290 to a point where it again may be split between two streams to either pass on to the product collection point 350 via conduit 292 or to recirculate via conduit 294 and valve 295 back through pump 296 and conduit 298 to optional blender 278 where the product stream may be again blended with fresh first reactant 3.

It should be noted that while the above description of a multiple stage apparatus includes descriptions of valves and conduits which make possible the recycling of portions of the product flow back to each reactor stage and which also make possible the blending of fresh first or second reactants at every stage, these options will rarely all be exercised simultaneously. Thus, it may be possible that no product will be recycled and no fresh first or second reactants added, with the subsequent stages merely acting as an extension of the reaction zone of the first stage. Alternatively, when stoichiometric equivalents of both reactants have been initially fed into the first stage, only the recycling of product may be carried out, without any additional amounts of either reactant added to the streams entering the subsequent stages of the apparatus. Finally, if a stoichiometric excess of one of the reactants is initially fed into the first stage, only significant amounts of the other reactant may be blended with the inlet streams to subsequent stages. However, even in such circumstances, it may be necessary to add to subsequent stages minor increments of even the reactant initially added in stoichiometric excess to the first stage.

As shown in the dotted lines in FIG. 4, connected respectively to reactors 100, 200, and 300, optional heat exchanger loops, each comprising a heat exchanger 316, and a pump 320, may be connected to one or more of the reactors to remove exothermic heat generated in any or all of the reactors as needed.

In the sulfonation of the methyl laurate (or other alkyl long chain esters), the sulfur trioxide to methyl laurate feed

ratio is between about 0.8 and 1.2 (preferably 1.05). The sulfonation reactor outlet temperature is between about 60 and 100° C. (preferably about 74–75° C.). The sulfonation pressure of the inlet is between about 250 and 350 psia ( $1.7 \times 10^6$  and  $2.4 \times 10^6$  pascal) preferably about 300–306 psia (about 2.1 and  $10^6$  pascal). The outlet pressure is between about 50 and 100 psia ( $3.4 \times 10^4$  and  $6.9 \times 10^4$  pascal), preferably about 65 psia ( $4.4 \times 10^4$  pascal). The residence time in the reactor is between about 1 and 4 sec. (preferably about 2.3 sec.). The conversion of methyl laurate is high, generally between about 90–99% (usually about 97–98%). The selectivity to produce alpha-sulfomethyl laurate is high, generally between about 90 and 99% (usually about 95–96%).

In one embodiment, a reactor of the present invention has an overall shell size of about 40–60 in (100–150 cm) in length, preferably about 45 in (114 cm), and a diameter of about 15–25 in (38–63 cm), preferably 19–20 in (48–51 cm). The number of porous tubes is between about 150 and 220 (preferably about 189–190). The porous tubes have between about 0.6–2.54 cm inside diameter (I.D.) (preferably about 1.6 cm) and an outside diameter (O.D.) of between about 1.27 and 3.8 cm, preferably about 2.2 cm. The reactor has between about 75 and 125 cm of active length, preferably about 100 cm. The mixing elements and mixing balls having a diameter of between about 0.5 and 0.1 cm, preferably about 0.25 cm.

#### Pulsatile Flow

In one embodiment referring to FIGS. 1 and 3, the exothermic reactor process uses, with the first reactant 3, a slurry of a catalyst 12A in reactor 10. The flow of catalyst slurry 12A with the mixing elements 12 occurs such that the flow rate of the first reactant 3 changes as a function of time. This flow rate change may be referred to as pulsatile (or pulsed) flow e.g. a sine wave, square wave, irregular wave, etc. The pulsed flow prevents the accumulation of solid catalyst particles 12A at fixed points on the mixing elements 12. This accumulation of catalyst particles 12A is not desired because it changes the flow characteristics in mixing in the reaction zone and may ultimately block the flow of catalyst or reactant or both.

Preferably, the pulsed flow changes with time in a cyclic manner. For instance, the rate of flow of catalyst slurry may change in the cycle from maximum flow to a level of about 80% of the maximum rate of flow. Preferably, the rate of flow of catalyst slurry cycles down to a level of about 50% of the maximum rate of flow of the catalyst slurry, then returns to the maximum flow rate. Preferably, the rate of flow of catalyst slurry cycles down to a level of about 20% in the reverse direction of the maximum rate of flow of the catalyst 12A, then returns to about the maximum flow rate in the original direction of flow.

In the pulsed flow, a typical example is the reaction of hydrogen with an alkene using a flowing slurry of Raney nickel catalyst particles suspended in the alkane. The maximum rate of flow of the reactant suspended catalyst corresponds to residence times of between about 0.5 to 6000 sec. The flow rate can change to achieve a rate of flow of between about 80% and ~20% ml/sec. of maximum. After remaining at this reduced flow rate (about 50% of maximum) for between about 0.1 and 1000 sec, the rate of flow is increased back to the maximum flow rate.

#### Separation (e.g., Evaporation) of Reaction Products

In one embodiment, the present invention is improved by removal of volatile reaction products. The volatile reaction products or reactants are those having a vapor pressure of about 1 mm of Hg or higher at the reaction temperature of the reaction of step (c). Referring now to FIGS. 2 and 8,



reactor 40 is one having a shell 60 and having multi tube porous barrier reactors 50. The second reactant 4 enters through inlet 62 via line 62A and is forced under pressure from the shell side through the porous barrier 52 into a recirculation stream of product 48A. The second reactant can be removed or recycled via line 64A at outlet 64. The first reactant is introduced to the reactor 60 via inlet 42 via line 42A in a continuous (or a pulsed) stream in the tube side of the reactor. A recycle loop of lines 48A and 48B, evaporator 500, and line 48D has a flash evaporator 500 to remove the volatile products of the reaction. The reaction products (or multiple components) is conveyed from outlet 48 via line 48A and 48B to an optional cooler 501 and then as a liquid via line 48B to the evaporator 500. The volatile reaction products are removed as a vapor via line 48C. The liquid product is conveyed via line 48D to line 42A, and then is recycled through the primary reactor 40. In effect, a steady state loop is created for maximum heat removal. The volatile reaction products are removed which prevents their further reaction and the formation of undesirable side products, and usually permits the operation of the primary reactor at higher temperatures, as compared to the system which does not have the evaporator, e.g. from about 5° C. up to about 200° C. higher than the reaction systems not having the evaporator.

The fields of use for the present invention include, but are not limited to, formation of a pesticide, a fungicide, a rodenticide, an insecticide, a herbicide, a pharmaceutical, a surfactant, a demulsifying agent, a fabric treatment agent, a hydrocarbon solvent, a hydrocarbon fuel, an organic polymer, a synthetic lubricant, a halogenated hydrocarbon, a fire retardant and the like.

Surfactants which are prepared according to the present invention, include but are not limited to, alkyl benzene sulfonates, linear alkylbenzene sulfonates, secondary alkane sulfonates, alpha olefin sulfonates, alkyl glyceryl ether sulfonates, methyl ester sulfonates, natural fat sulfonates, alcohol sulfates, alcohol ether sulfates and the like.

The following examples serve to further explain and describe the present invention. They are not to be construed to be limiting in any way.

#### EXAMPLE I

##### Ester Sulfonation (SO<sub>3</sub> High Flow Rate)

(a) Fresh methyl laurate, having a viscosity of 2 cp, may be fed at a rate of 550 grams/sec into a mixer where it is mixed with a 5650 grams/sec flow of recycled product and the resulting mixture is fed, at a temperature of about 38° C. (-100° F) and a pressure of about 340 psia ( $2.3 \times 10^6$  pascal (where 1 psia=6894.7 pascal)) into the top of 85 porous wall tubes arranged vertically in a bundle in a cylindrical reactor having an inside diameter (ID) of about 20 in. (50.8 cm). Each tube has an ID of about  $\frac{3}{4}$ " (1.91 cm), and has a 110 cm. length of porous metal comprising stain-less steel fabricated by powder metallurgy to have a nominal pore size of generally about 0.2 microns ( $\mu$ meters) and a viscosity normalized permeance of about 0.0037 cm<sup>3</sup> cp/cm<sup>2</sup> sec psi.

The tubes are each packed with inert glass balls, each having a diameter of 0.320 cm., up to a distance of 10 cm. above the porous portion of each tube and also extending to the bottom of each tube, i.e., beyond the porous portion of the tube in the direction of reactant flow.

On the shell side of the reactor, 205 grams/second of liquid SO<sub>3</sub> may be mixed with a 760 grams/sec flow of recycled product at a temperature of about 38° C. (-100° F) and a pressure of about 350 psia ( $2.4 \times 10^6$  pascal) and fed

into the shell portion of the reactor to pass through the porous tubes and react with the methyl laurate therein.

The resulting product stream, leaving the reactor at a temperature of about 74° C. (-165° F) and a pressure of about 65 psia ( $4.5 \times 10^5$  pascal), is fed through a heat exchanger containing 1350 tubes having an ID of 1.91 cm and 240 cm in length, and also packed with 0.32 cm diameter inert glass balls.

The sulfonated methyl laurate product from such a reactor system will be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology. This is because there is no temperature peak typical of the entry region of a falling film reactor and because there is even distribution of reactant all along the reactor length in the process of the invention.

(b) Similarly, the reaction described in Example 1(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene, the corresponding linear alkylbenzenesulfonic acid is obtained. These are useful as surfactants.

(c) Similarly, the reaction described in Example 1(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, and the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

#### EXAMPLE II

##### Ester Sulfonation (SO<sub>3</sub> Lower Flow Rate)

(a) Fresh methyl laurate, having a viscosity of 2 cp, may be fed at a rate of 550 grams/second into a mixer where it is mixed with a 6400 grams/sec flow of recycled product and the resulting mixture is fed, at a temperature of about 38° C. (-100° F) and a pressure of about 265 psia ( $1.8 \times 10^6$  pascal) into the top of 125 porous wall tubes arranged vertically in a bundle in a cylindrical reactor having an ID of about 20 inches. Each tube has an ID of about  $\frac{3}{4}$ " (1.91 cm), and has a 110 cm. length of porous metal comprising stainless steel fabricated by powder metallurgy and coated with zirconia to have a viscosity normalized permeance of about  $1.2 \times 10^{-5}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi.

The tubes are each packed with inert glass balls, having a diameter of 0.320 cm., up to a distance of 10 cm. above the porous portion of each tube and also extending to the bottom of each tube, i.e., beyond the porous portion of the tube in the direction of reactant flow.

On the shell side of the reactor, liquid SO<sub>3</sub> may be introduced into the reactor, without mixing with recycled product, at a flow rate of about 205 grams/sec flow, and at a temperature of about 38° C. (-100° F), and a pressure of about 350 psia ( $2.4 \times 10^6$  pascal) to pass through the porous tubes and react with the methyl laurate therein.

The resulting product stream leaving the reactor at a temperature of about 74° C. (-165° F) and a pressure of about 65 psia ( $4.5 \times 10^5$  pascal) is fed through a heat exchanger similar to that described in Example I. The resulting sulfonated methyl laurate product will again be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

(b) Similarly, the reaction described in Example II(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene, the corresponding linear alkylbenzenesulfonic acid is obtained.

(c) Similarly, the reaction described in Example II(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, and the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

### EXAMPLE III

#### Ester Sulfonation, Multiple Stages

(a) To illustrate the use of multiple stages of the process of the invention, when products with particularly low levels of impurities are desired, three shell and tube reactors similar to those used in Examples I and II may be used. The porous wall portion of each tube would be 110 cm in length and the inner diameter of each would be 1.91 cm (0.4"). The porous portion of each tube may be fabricated from a stainless steel powder metallurgy and coated with zirconia to provide a viscosity normalized permeance of  $1.2 \times 10^{-5}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi and each tube could be filled with 0.32 cm diameter inert glass balls to 10 cm above and below the porous portion of the tube. In each reactor, the tubes would be located in a 50.8 cm (20 in) diameter shell. Each reactor may be connected to a heat exchanger having tubes with a diameter of 1.91 cm ID filled with the same inert 0.32 cm diameter spherical glass mixing elements used in the reactors. The length of the tubes could be varied for different stages.

In the first stage, a 550 grams/sec flow of fresh methyl laurate may be mixed with 2900 grams/sec of cooled recycled product from the first stage and introduced into a 46 tube reactor first stage at a temperature of 38° C. (100° F) and a pressure of 155 psia ( $1.1 \times 10^6$  pascal).

About 50% (103 grams/sec) of the total SO<sub>2</sub> is introduced as a liquid into the shell side of the first stage reactor at 350 psia and a temperature of 38° C. The resultant product flow, having a temperature of about 74° C. (165° F) and a pressure of 65 psia ( $4.5 \times 10^5$  pascal), is fed into a heat exchanger containing 45 of the 0.6 meter long tubes filled with mixing elements.

From the output of the first stage heat exchanger, 655 grams/sec is mixed with 1775 grams/sec of cooled product stream from the second stage and fed into 36 tubes comprising the second stage reactor at a temperature of 38° C. (100° F) and 200 psia ( $1.4 \times 10^6$  pascal). The other 2900 grams/sec of cooled product from the first stage may be recycled back to the first stage reactor as described above.

About 35% (72 grams/sec) of the total amount of SO<sub>2</sub> is introduced as a liquid into the shell side of the second stage reactor at 350 psia ( $2.4 \times 10^6$  pascal) which will result in a product flow exiting the second stage reactor at 65 psia ( $4.5 \times 10^5$  pascal) and a temperature of 74° C. (165° F). This product flow is then cooled by feeding it into 115 1.3 meter long mixing element-filled tubes in the second stage heat exchanger.

From the second stage recirculating loop downstream of the second stage heat exchanger, 725 grams/sec of product flow is mixed with 320 grams/sec of cooled product from the third stage and introduced into the 19 tube third stage reactor at a temperature of 38° C. (100° F) and a pressure of 265 psia ( $1.8 \times 10^6$  pascal). In this stage the remaining 15% of the SO<sub>2</sub> is introduced at a temperature of 38° C. and a pressure of 115 psia ( $1.1 \times 10^6$  pascal).

The product flow from the third stage reactor tubes leaves the reactor at 65 psia and 74° C. (165° F) and enters a heat exchanger containing 200 of the 2.3 meter tubes which are also filled with mixing elements. From the recirculating loop

coming from this third heat exchanger, 760 grams/sec of product are withdrawn, while the remaining 320 grams/sec of cooled product are recycled as previously described.

The resulting sulfonated methyl laurate product will again be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

(b) Similarly, the reaction described in Example III(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene, the corresponding linear alkylbenzenesulfonic acid is obtained.

(c) Similarly, the reaction described in Example III(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, and the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

### EXAMPLE IV

#### Ester Sulfonation, Small Temperature Increase

(a) To illustrate a modification of the process of the invention, where all of the SO<sub>2</sub> is introduced in one stage with a very low rise in temperature because of the high recycle rate, and a second stage is provided operating at a substantially higher temperature to allow any rearrangement of SO<sub>2</sub> among the molecules in the product from the first reactor stage, methyl laurate may be introduced into a reactor containing 200 tubes, each having the same dimensions and viscosity normalized permeance as in Example II.

The flow rate of fresh methyl laurate is also the same as in Example II, i.e., 550 grams/sec, but the amount of recycled product blended with the methyl laurate prior to introduction into the tubes is 10,750 grams/second, i.e., much higher than Example II, resulting in more thermal mass and, therefore, a commensurate reduction in the temperature rise from the fixed exothermic heat generated. The combined stream enters the tubes of the reactor at 38° C. (100° F) and 285 psia ( $1.96 \times 10^6$  pascal).

On the shell side of the reactor a stream of 205 grams of liquid SO<sub>2</sub> is introduced into the reactor at a temperature of 38° C. (100° F) and a pressure of 290 psia ( $2.0 \times 10^6$  pascal).

The product flow exiting the reactor then is circulated through the same mixing element-filled heat exchanger as in Example I and a product flow of about 760 grams/sec is withdrawn from output of the heat exchanger (with the balance recycled back to the reactor), mixed with a flow of about 5000 grams/sec of recycled product from a mixing tank, and pumped to the tube side of a heat exchanger where it is heated to have an exit temperature of 82° C. (180° F). This flow goes to the mixing tank which is sized to have a residence time of about 15 minutes. This time at elevated temperature allows any rearrangement of the materials in the product to closely approach equilibrium. The product is continuously withdrawn from the mixing tank at 760 grams/sec and cooled for storage or use.

In this regard, it should be noted that such a mixing tank is filled with the product from the last operation. The first time the apparatus is started, the tank is filled from the low temperature reactor. The mixing tank can have any type of stirring or agitation means within it, including mixing elements. For example, some molecules could contain two attached SO<sub>2</sub> groups and other molecules have no SO<sub>2</sub> groups attached. The breaking of a SO<sub>2</sub> group away from a molecule with two such groups and the combination of an SO<sub>2</sub> group with a molecule without an SO<sub>2</sub> group on it would not generate substantial net heat in the mixing tank.

Again, the resulting product will be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

(b) Similarly, the reaction described in Example IV(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene the corresponding linear alkylbenzenesulfonic acid is obtained.

(c) Similarly, when the reaction described above in Example IV(a) is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

#### EXAMPLE V

##### Alcohol and Ethylene Oxide

(a) Fresh tridecyl alcohol, having a viscosity of 1 cp, may be fed at a rate of 270 grams/second into a mixer where it is mixed with a 12,300 grams/sec flow of recycled product and the resulting mixture is fed, at a temperature of about 121° C. (-250° F) and a pressure of about 80 psia ( $5.5 \times 10^5$  pascal) into the top of 585 porous wall tubes arranged vertically in a bundle in a cylindrical reactor having an ID of about 30 inches. Each tube has an ID of about  $\frac{1}{8}$ " (1.59 cm), and has a 100 cm. length of porous metal comprising stainless steel fabricated by powder metallurgy and coated with zirconia to have a viscosity normalized permeance of about  $1.2 \times 10^{-5}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi.

The tubes are each packed with inert glass balls, having a diameter of 0.265 cm., up to a distance of 10 cm. above the porous portion of each tube and also extending to the bottom of each tube, i.e., beyond the porous portion of the tube in the direction of reactant flow.

On the shell side of the reactor, gaseous ethylene oxide may be introduced into the reactor, without mixing with recycled product, at a flow rate of about 532 grams/sec flow, and at a temperature of about 121° C. (-250° F), and a pressure of about 250 psia ( $1.7 \times 10^6$  pascal) to pass through the porous tubes and react with the tridecyl alcohol therein.

The resulting product stream leaving the reactor at a temperature of about 199° C. (-300° F) and a pressure of about 65 psia ( $4.5 \times 10^5$  pascal) is fed through a heat exchanger similar to that described in Example 1. The resulting ethoxylated tridecyl alcohol product will have a very unitary product distribution and be low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

Thus, the present invention provides a process for carrying out a process wherein the flow of second reactant into the reaction zone is controlled, to thereby control the reaction and the amount of heat generated, by the use of a porous barrier which restricts the amount of second reactant flowing across the porous barrier into the reaction zone. Such control of the reaction and control of heat, while providing adequate mixing of the reactants in the reaction zone to ensure homogeneous reaction and heat generation in the reaction zone, results in a product which, as mentioned above in the examples, is uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art of chemical processing and control of reaction in a reaction zone by use of a porous barrier between a first reactant and a second reactant having

mixing elements in the reaction zone as described herein. The use of a porous barrier and mixing elements in chemical processing applications is such that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the present invention. In addition, many modifications may be made to adapt a particular situation, material, or composition of matter, process, process step or steps, or the present objective to the spirit and scope of this invention, without departing from its essential teachings.

#### We claim:

1. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

- (a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;
  - (b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said second reactant; and
  - (c) maintaining the pressure within said second reaction zone higher than the pressure in said first reaction zone at said porous wall, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;
- whereby said one or more second reactants will pass through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof.
2. The process of claim 1 wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi.
  3. The process of claim 1 wherein a portion of the product flow from said reactor is recycled back and blended with said one or more first reactants being fed into said first reactor zone.
  4. The process of claim 3 wherein said product flow from said reactor is first passed through a heat exchanger before said portion of said product flow is recycled back and blended with said one or more first reactants being fed into said first reactor zone.
  5. The process of claim 1 wherein a portion of the product flow from said reactor is recycled back and blended with said one or more second reactants being fed into said second reactor zone.
  6. The process of claim 5 wherein said product flow from said reactor is first passed through a heat exchanger before said portion of said product flow is recycled back and blended with said one or more second reactants being fed into said second reactor zone.
  7. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

- (a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;
- (b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor

zone by a porous wall capable of being penetrated by said second reactant; and

- (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;

whereby said one or more second reactants will pass through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof, wherein at least one of said reactants is a liquid.

8. The process of claim 7 wherein at least one of said one or more said first reactants is a liquid.

9. The process of claim 7 wherein at least one of said one or more second reactants is a liquid.

10. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

- (a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;
- (b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said second reactant; and

- (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;

whereby said one or more second reactants will pass through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof;

wherein at least one of said one or more first reactants is a liquid and at least one of said one or more second reactants is a liquid.

11. The process of claim 1 wherein the temperature of each of said reactants being fed into the respective reaction zones is within a range of from about  $-50^{\circ}\text{C}$ . to about  $500^{\circ}\text{C}$ .

12. The process of claim 1 wherein the pressure of each of said first reactants and said second reactants being fed into the respective reaction zones is within a range of from about 14 psia to about 1000 psia, with the pressure of said one or more second reactants being greater than the pressure of said one or more first reactants.

13. The process of claim 1 wherein all or a portion of said product is recycled back to said first reactor zone.

14. The process of claim 13 wherein all or a portion of said product is cooled and then recycled back to said first reactor zone.

15. The process of claim 1 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reaction zone.

16. The process of claim 1 wherein the process is selected from the group consisting of oxidation, sulfonation, hydrogenation, halogenation, ethoxylation, sulfation, nitration, and polymerization.

17. The process of claim 1 wherein the flow of the first reactant is pulsed.

18. The process of claim 1 wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;

- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) creating a reaction product liquid; and

- (f) optionally recycling all or a portion of the reaction product liquid now depleted of volatile reactants, volatile reaction products or a combination thereof to the first reactor zone of step (a).

19. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

- (a) feeding into a first reactor zone containing mixing elements therein one or more first reactants at a first pressure;

- (b) feeding one or more second reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said one or more second reactants; and

- (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;

whereby said one or more second reactants will pass through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid having mixing elements therein.

20. The process of claim 19 wherein said mixing elements in said first reactor zone have at least one dimension equal to from about  $\frac{1}{4}$  to about  $\frac{1}{100}$  of the largest cross sectional dimension of said first reactor zone measured in the direction which is perpendicular to the flow of said one or more first reactants through said first reactor zone.

21. The process of claim 20 wherein said mixing elements in said first reactor zone have at least one dimension equal to from about  $\frac{1}{5}$  to about  $\frac{1}{10}$  of the largest cross sectional dimension of said first reactor zone measured in the direction which is perpendicular to the flow of said one or more first reactants through said first reactor zone.

22. The process of claim 19 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reaction zone.

23. The process of claim 19 wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;

- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) producing a reaction product liquid; and

- (f) optionally recycling all or a portion of the reaction product liquid now depleted of volatile reactants, volatile reaction products or a combination thereof to the first reactor zone of step (a).

24. An exothermic process for forming a reaction product fluid by reaction of one or more first liquid reactants with one or more second liquid reactants, which process comprises:

- (a) feeding one or more first liquid reactants at a first pressure through a first reactor zone having mixing elements therein;
  - (b) feeding one or more second liquid reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said one or more second liquid reactants; and
  - (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;
- whereby said one or more second liquid reactants will pass through said porous wall to contact said one or more first liquid reactants in said first reactor zone and form said reaction product fluid having mixing elements therein.

25. The process of claim 24 wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;
- (e) separating volatile reactants or reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) producing a reaction product liquid; and
- (f) optionally recycling all or a portion of the reaction product liquid now depleted of volatile reactants, volatile reaction products or a combination thereof to the first reactor zone of step (a).

26. The process of claim 24 wherein said mixing elements in said first reactor zone have at least one dimension equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest cross sectional dimension of said first reactor zone measured in the direction which is perpendicular to the flow of said one or more first reactants through said first reactor zone.

27. An exothermic process for forming a reaction product fluid by reaction of one or more liquid first reactants with one or more second reactants, at least one of which is gaseous at standard temperature and pressure, which process comprises:

- (a) feeding said one or more liquid first reactants at a first pressure through a first reactor zone having mixing elements therein;
- (b) feeding said one or more second reactant, at least one of which is gaseous at ambient conditions, at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said one or more second reactants; and
- (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;

whereby said one or more second reactants will pass through said porous wall to contact said one or more liquid first

reactants in said first reactor zone and form said reaction product fluid having mixing elements therein.

28. The process of claim 27 wherein said mixing elements in said first reactor zone have at least one dimension equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest cross sectional dimension of said first reactor zone measured in the direction which is perpendicular to the flow of said one or more liquid first reactants through said first reactor zone.

29. The process of claim 27 wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) producing a reaction product fluid; and
- (f) optionally recycling all or a portion of the reaction product liquid now depleted of volatile reactants, volatile reaction products or a combination thereof to the first reactor zone of step (a).

30. The process of claim 27 wherein said porous wall through which said one or more second reactants pass into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2}$  cm<sup>2</sup> cp/cm<sup>2</sup> sec psi.

31. The process of claim 30 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reactor zone.

32. An exothermic process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants which comprises:

- (a) feeding a first reactant at a first pressure through a first reactor zone containing mixing elements having at least one dimension equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone measured in the direction which is perpendicular to the flow of said first reactant through said first reactor zone;
- (b) feeding a second reactant at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said second reactant; and
- (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction product fluid or combinations thereof in said first reactor zone through said porous wall from said first reaction zone to said second reaction zone;

whereby said second reactant will pass through said porous wall to contact said first reactant in said first reactor zone and form said reaction product fluid.

33. The process of claim 32 wherein at least one of said reactants is a liquid.

34. The process of claim 32 wherein said porous wall through which said second reactant passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $10^{-4}$  cm<sup>2</sup> cp/cm<sup>2</sup> sec psi.

35. The process of claim 32 wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants

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or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) producing a reaction product liquid; and

- (f) optionally recycling all or a portion of the reaction product liquid now depleted of volatile reactants, volatile reaction products or a combination thereof to the first reactor zone of step (a).

36. A process for forming a reaction product fluid by reaction of a first liquid reactant with a second liquid reactant, which process comprises:

- (a) feeding a first liquid reactant at a first pressure into a first reactor zone containing particles having at least one dimension equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest cross sectional dimension of said first reactor zone measured in the direction which is perpendicular to the flow of said liquid reactant through said first reactor zone;

- (b) feeding a second liquid reactant at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said second liquid reactant; and

- (c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone, to thereby inhibit any flow of said one or more first reactants, said one or more second reactants, said reaction

product fluid or combinations thereof in said first reactor zone through said

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porous wall from said first reaction zone to said second reaction zone;

whereby said second liquid reactant will pass through said porous wall to contact said first liquid reactant in said first reactor zone and form said reaction product fluid comprising a liquid, a gas, or combinations thereof.

37. The process of claim 36 wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product of step (c) to an evaporator;

- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) producing a reaction product liquid; and

- (f) optionally recycling all or a portion of the reaction product liquid now depleted of volatile reactants, volatile reaction products or a combination thereof to the first reactor zone of step (a).

38. The process of claim 36 wherein said porous wall through which said second liquid reactant passes into said first reactor zone has a viscosity normalized permeability ranging from about  $5 \times 10^{-6}$  to about  $5 \times 10^{-8}$  cm<sup>2</sup> cp/cm sec.

39. The process of claim 38 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reactor zone.

\* \* \* \* \*



US006127571A

**United States Patent** [19]**Mulvaney, III**[11] **Patent Number:** **6,127,571**[45] **Date of Patent:** **Oct. 3, 2000**[54] **CONTROLLED REACTANT INJECTION  
WITH PERMEABLE PLATES**[75] **Inventor:** Robert C. Mulvaney, III, Arlington Heights, Ill.[73] **Assignee:** UOP LLC, Des Plaines, Ill.[21] **Appl. No.:** 08/999,877[22] **Filed:** Nov. 11, 1997[51] **Int. Cl.<sup>7</sup>** ..... C07C 309/00[52] **U.S. Cl.** ..... 562/98; 562/99[58] **Field of Search** ..... 562/98, 99[56] **References Cited****U.S. PATENT DOCUMENTS**

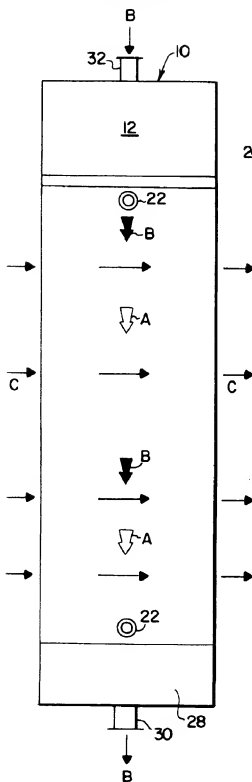
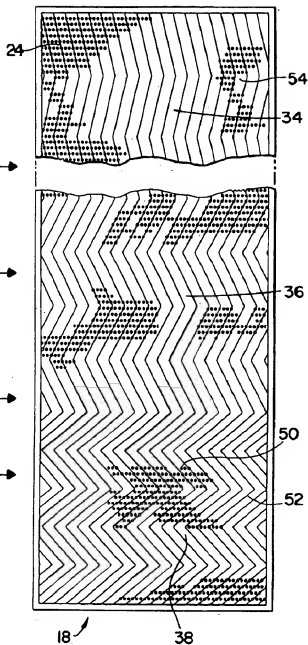
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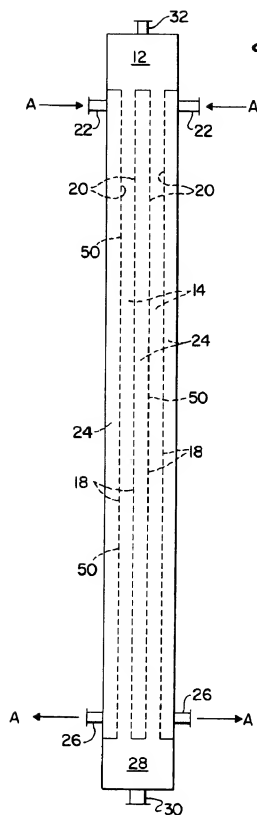
**ABSTRACT**

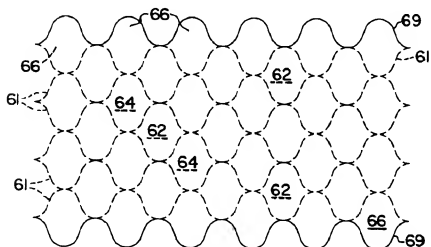
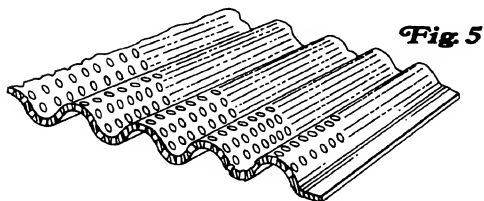
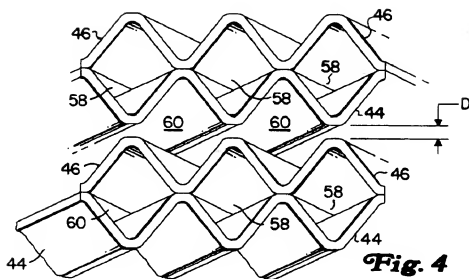
An arrangement for a fluid distributor-reactor type reactor uses perforated plates to circulate two reactants in alternate channels defined by spaces between parallel stacked plates to perform controlled distribution and mixing simultaneously with optional indirect heat transfer. One reactant enters one set of channels that serve as reaction channels. A set of second channels interleaved with the reaction channels serve as distribution channels that also provide a heat exchange function. Finely dispersed openings in the perforated plates distribute the reactant at low concentration from the distribution channels into the reaction channels. Dispersion of the reactant through the perforations will enhance the turbulence that is primarily introduced by the corrugated plates to insure good mixing of the reactants in the reaction channels. The pattern and size of the holes on the perforated plates may be varied as desired to disperse a carefully controlled amount of fluid across the plates over a large surface area. By maintaining a low addition rate of injected fluid reactant over the contact area, the concentration of the added reactant in the reaction channels may be kept as low as desired. The plates are preferably corrugated to introduce increased turbulence for promoting better distribution and dispersion of the fluids as one fluid is injected across the perforations. The corrugation angles can also be varied to suit the fluid flow properties of the fluid reactant and in particular varied over the height of the contacting zone to vary fluid residence time over different parts of the plates.

**12 Claims, 3 Drawing Sheets**

**Fig. 1****Fig. 2**







# 1 **CONTROLLED REACTANT INJECTION WITH PERMEABLE PLATES**

## FIELD OF THE INVENTION

This invention relates generally to the interaction of the dispersal and mixing of one reactant stream into another. More specifically this invention relates to the use of plate structures for distribution, contacting and mixing of reactants.

## BACKGROUND OF THE INVENTION

Certain chemical reactions are highly sensitive to the contacting conditions under which the reactants are brought together. Contacting conditions that can have a profound effect on the production of products in some reactions include physiochemical conditions such as reaction time, reagent concentration, reagent dispersion and temperature conditions. An example of a highly sensitive process of this type is the sulfonation of various compounds with a sulfonating agent. The initially formed sulfonates indicate a relatively high thermodynamic instability. It is well known that mild sulfonation conditions including short reaction times and low concentration gradients yield different products when compared to more drastic operating conditions.

A common method of controlling the contact between reactants in a reaction that is highly sensitive to process conditions is by the use of a thin film or falling film reaction zone. Falling film evaporators and reactors are well known in the art and are readily available commercially. Falling film evaporators pass a thin film of a liquid stream down one side of a heat exchange surface in indirect heat exchange with a heating medium that contacts an opposite side of the heat exchange surface and causes an at least partial evaporation of the falling liquid. Falling film reactors comprise a plurality of tubes or plates over which a thin film of one reactant is dispersed for countercurrent or cocurrent contact with a gaseous reactant stream. In the case of evaporation or reaction laminar flow layers in the thin film can inhibit heat transfer and diffusion of vapor.

One of the most well known falling film reactor arrangements is for the continuous sulfonation or sulfation of fluid state organic substances by reaction with sulfur trioxide (sulfuric anhydride) ( $\text{SO}_3$ ). In traditional falling film arrangements, the  $\text{SO}_3$  or other reactant is kept in a gaseous state. The reaction of the  $\text{SO}_3$  with the organic substances is strongly exothermic throughout the reaction which occurs rapidly or in many cases goes nearly instantaneously to completion. The gaseous  $\text{SO}_3$  is normally diluted with air or other inert gases to a reduced concentration of 4-15 wt % which attenuates the severity of the reaction. The provision of cooling to the falling film contact surfaces also avoids the generation of temperature peaks from the highly exothermic reaction.

U.S. Pat. No. 3,925,441 issued to Toyoda et al. describes the use of flat plates for falling film sulfonation.

U.S. Pat. No. 5,445,801 to Pisoni describes a tube arrangement for falling film sulfonation that provides improved liquid distribution and accommodates expansion of the tubes.

U.S. Pat. No. 4,059,620 issued to Johnson describes the advantages of maintaining a desired heat exchange profile during the sulfonation of organic compounds with sulfur trioxide.

The sulfonation or reaction of other organic compounds can cause extensive side reactions. Side reactions are best

minimized by a uniform distribution of the falling liquid with gaseous reactants over the contact surfaces. Perhaps more important is the need to keep the sulfonating compound in relatively low concentration. Systems for controlling the distribution of liquid into tubes or plate arrangements for falling film reactors include: weir and dam systems and slit or orifice arrangements that can be mechanically adjusted in various ways. Nevertheless, minor irregularities in the delivery systems to the top of the falling film apparatus can result in substantial flow variations with the attendant drawback of side reaction production. In addition to the problems associated with uniform delivery to a falling film contact surface, variations in the surface also create flow irregularities that can lead to non-uniform contacting and promote side reaction production.

The systems that use a gaseous phase reactant to contact the wetted walls of the falling film reactor also have the disadvantage or requiring a large circulation of gas in addition to the circulation of the liquid phase material down the walls of the reactor and the circulation of a cooling fluid. Care must be taken to control the concentration of the gaseous reactant in the gas phase. As a result the gas phase reactant is typically diluted with another gas to maintain a low reactant concentration and avoid unwanted by-product formation. For example in the sulfonation of aromatic hydrocarbons, a film of aromatic hydrocarbon is passed down the walls of channels through which an air stream containing dilute  $\text{SO}_3$  circulates. Supplying the air stream requires continual drying of large quantity of air if the air passes once through the channels. Recirculation of the air ordinarily necessitates purification to prevent product re-entrainment which will cause by-product formation.

The use of a permeable wall to introduce reagents into reaction zones is disclosed in U.S. Pat. No. 3,375,288. It is known to carry out a sulfonation reaction with liquid phase reagents in a reaction zone that has fluid permeable walls. An article attributed to the Stanford Research Institute and published in the June 1996 issue of Chemical Engineering Magazine and U.S. Pat. No. 5,503,240 discloses the passing of a sulfonation agent through permeable tubes that are surrounded by the sulfonation substrate. The tubes have a low permeability that maintains the sulfonating agent in low concentration. The tubes contain a packing of particulate material to provide the required good mixing of the sulfonating agent that permeates the tube wall.

A reactor system is sought that will eliminate the need for diluent gas addition or recirculation, reduce boundary layer limitations in the dispersion of a reagent in low concentrations in a liquid contactors, overcome any initial maldistribution of liquid reactants in a liquid phase contactor, avoid the need for internal packing and facilitate the control of reaction temperature by promoting indirect heat transfer.

## SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide an apparatus and process for a fluid contactor that continually redistributes reactants.

Another object of this invention is to provide a fluid reactant contactor that facilitates good distribution and dispersion while promoting thorough mixing of the dispersed compound into a reagent.

A yet further object of this invention is to provide good distribution and dispersion of reaction fluids while simultaneously facilitating indirect heat exchange.

These and other objectives are achieved by an arrangement for a fluid distributor contactor type reactor that uses

plates containing permeable or perforated portions. The arrangement circulates the two reactants in alternate channels defined by spaces between parallel stacked plates. One reactant enters one set of channels that serve as reaction channels. A set of second channels, interleaved with the reaction channels, serve as distribution channels that can also provide a heat exchange function. Finely dispersed openings or permeation sites in the perforated plates distribute one reactant at low concentration from the distribution channels into the reaction channels. Dispersal of the reactant through the plate will introduce turbulence and promote good mixing of the reactants in the reaction channels. The pattern and size of the holes or permeable sections on the perforated plates may be varied as desired to disperse a carefully controlled amount of fluid across the plates over a large surface area. By maintaining a low addition rate of injected fluid reactant over the contact area, the concentration of the added reactant in the reaction channels may be kept as low as desired. Pressure drop across the perforated plate may be controlled to attain the desired degree of reactant penetration into the reaction channels. In liquid phase systems the addition of the reactant directly into the reaction channels eliminates the gas medium and any need for the associated recycle, separation or drying that were part of falling film contacting.

It is also useful to provide the perforated plates with a form or projections that increase the turbulence in the reaction channels. Such forms can include pins, rods or tabs extending outward from the plates to mildly agitate the flow through the reaction channels. Such flow agitation should be kept below a level that will cause substantial variation in the residence time of reactant through the reaction channels. A preferred plate form for introducing turbulence use corrugated plates that are stacked next to or in close proximity to each other to create the reactant and distribution flow channels.

The distribution channels that supply the liquid reactant to the perforations can also provide the passageways for indirect heat exchange of the reactant and product fluid in the reaction channels with the fluid in the distribution channels on the opposite side of the plates. A large excess volume of the second reactant normally circulates through the heat exchange channels to provide sufficient heating or cooling with only a small amount of the fluid reactant passing through the perforations for reaction in the reaction channels. The reactant is preferably circulated through the distribution channels at a much higher circulation rate than the dispersal rate of fluid across the reaction channels. Thus the reactant circulates at a high rate in the distribution channels as an optional indirect heat transfer fluid. Preferably the perforated plates will have a shape or form that promotes a high degree of heat transfer between the distribution and the reaction channels. Thin wall, relatively flat plates provide the best heat transfer characteristics. Again turbulence introducing forms or structures for the perforated plates are again beneficial for the heat transfer as well as the mixing functions. Corrugated plates are the preferred turbulence introducing form for both heat transfer and mixing. The injection of the reactant fluid from the heat exchange channels when performed with sufficient pressure drop provides velocity that also aids in creating turbulence.

The corrugations on the preferred form of the plates can be varied to suit the fluid flow properties of the fluid and in particular may be varied over the height of the contacting zone to vary fluid residence time and turbulence over different parts of the plates. The corrugated plates may be spaced apart to increase the flowing volume in either the

reactant or distribution channels but preferably make contact with each other to provide structural stability. Turbulence introduced by the corrugated plates will again facilitate indirect heat transfer between the reactants in the distribution and reaction channels. In this manner the corrugated plate arrangement provides advantages for the dispersion, the contacting, the mixing and the heating or cooling of fluids in the reaction channels and in and between the reaction and distribution channels.

Accordingly, in a broad process embodiment this invention is a process for the reaction of a fluid stream by the controlled addition of a fluid reactant. The process passes a first stream comprising a reactive fluid into a plurality of reaction channels defined by a first side of a plurality of stacked plates. A second stream comprising a reactant fluid circulates through a plurality of distribution channels defined by a second side of the plates to supply a reactant fluid and optionally to provide indirect heat exchange with the reactive fluid. Permeable portions distributed over the surface of the plates to control the contact of the reactant fluid with the reactive fluid distribute a portion of the reactant fluid into the reaction channels. The process recovers a reaction product from the reaction channels.

More specific process embodiments deal with the manner of distributing fluid and the specific fluid components and reactions. One such reaction is the sulfonation of a substrate with sulfur trioxide. Another reaction could be the contacting of a subcooled ethylene oxide containing liquid with an organic material to perform ethoxylation.

In an apparatus embodiment this invention is a reactor for the controlled distribution of reactants. The reactor includes a plurality of contacting plates, containing perforation or permeable sections, stacked adjacent to one another to define reaction channels between the first sides of adjacent plates. Means are provided for passing a first fluid into the reaction channels. A distribution channel located between each reaction channel and defined by the second side of the plates distribute a second fluid through the plates and optionally circulate the second fluid as an indirect heat exchange medium. Means are provided for supplying the second fluid to the distribution channels and for collecting a fluid stream containing a reaction product from the reaction channels.

This invention may use any type of plate to define the alternate reaction and distribution channels. Preferred plates for this invention are those that will enhance the distribution of the fluid reactant that is injected through the plates into contact with the other liquid stream. The plate surface can enhance the intermixing of components by introducing additional turbulence to the surface of the plate defining the reaction channels. The turbulence should be enough to intermix the different fluids but not so great as to cause extensive backmixing of the fluids that can lead to non-uniform contacting and by-product generation. Corrugated plates with corrugations extending transverse to the direction of fluid circulation can be particularly beneficial in this regard.

In particular, corrugations on the contacting plates can be varied to suit the particular characteristics of the process and fluids employed. For low surface tension and low viscosity fluids, a relatively horizontal and shallow pitched corrugation is most beneficially employed. A slight downward pitch may be provided on the horizontal corrugations to provide a transverse movement when a liquid phase is present. The corrugation sections are preferably in a herring bone pattern so that the fluid flows back and forth in a horizontal direction

across the reactor as it moves downwardly over the reactor thereby increasing the redistribution and uniformity of the flow. The number and height of corrugation rows can be varied in order to increase the dispersion of the fluids passing along the corrugations. In the case of liquids, as the viscosity of the liquid reactants increases, the slope of the corrugations and depth of the corrugations may be increased to provide additional redistribution and turbulence.

Controlled addition of the fluid reactant into the reaction channel is accomplished by distributing a portion of the fluid from the distribution channels across the plates through permeable sites that extend over a large area of the plates. When the contactor is used to provide an indirect heat exchange function, a relatively small amount of the fluid circulating in the distribution channels, usually less than 10% of the total circulating fluid, will normally pass through the permeable portions of the plate into contact with the fluid in the reaction channels films. More typically the amount of fluid passing through the plates will be less than 5% of the total circulating fluid entering the distribution/heat exchange channels.

Any type of structure may be used to provide the permeable sections of the plates. In simplest form the plates will contain a widely dispersed array of relatively fine perforations. The size and number of the perforations will of course depend on the fluid properties at the desired operating conditions. Fluid phase will typically be the most important fluid property. The invention can use all liquid phase fluids all gas phase fluids or may inject a liquid phase into a gas phase or a gas phase into a liquid phase. Other important fluid properties are the desired concentration of the fluid in the reaction channels and the pressure drop across the plates. In reactions such as sulfonation the perforations will ordinarily be in a size range of from 0.1 mm to 1 mm and will create about 5-10% open area across the plates. It may be desirable to decrease the density or size of perforation in the lower portions on the plates as more of the fluid in the reaction channels has been converted to product and need for additional reactant injection diminishes.

The multitude of perforations can have the added advantage of again introducing a desired degree of turbulence. Pressure drop across the plates may be regulated to further control turbulence. A low pressure drop prevents the formation of extended fluid jets. Relatively high pressure drops are generally preferred to provide additional turbulence and further enhance mixing. High pressure drops may be particularly preferred where the fluid phases differ and a large jet may be desirable to force injected reactant gas across a liquid reactive stream. High pressure drop may also atomize a reactant liquid as it mixes with a reactive gas stream. Suitable pressure drops will vary widely depending of the fluid properties and the size of the perforations.

Suitable plate elements for this invention may also have a composite construction wherein a permeable material is incorporated onto the plates between the channels over holes in the plate. The permeable material can comprise an ultra-fine screen that inhibits any jet creation as liquid passes through the plate. Exposure of the circulating liquid to a fine screen material can introduce the desired turbulence and the well dispersed area of permeable sections over the plate while the plate provides the necessary support of the screen material. Permeable membranes or other coatings across perforations would also provide a useful structure, especially for the control of gas phase flow, but are not preferred when performing simultaneous heat exchange since their insulating effects may interfere with the indirect heat transfer across the plate.

Additional details, embodiments, and arrangements of this invention are described in the following "detailed description of the invention."

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing a plate reactor of this invention and possible directions for process flow streams.

FIG. 2 is a schematic diagram of a corrugated plate for the liquid-liquid contacting of this invention.

FIG. 3 is a schematic cross-section of a reactor arranged in accordance with this invention.

FIG. 4 is a three-dimensional view of a portion of the contacting and heat exchange channels of this invention shown with perforation omitted.

FIG. 5 is a schematic diagram of a perforated plate for the heat transfer channels of this invention.

FIG. 6 is a schematic cross-section of channels arranged in accordance with this invention.

## DETAILED DESCRIPTION OF THE INVENTION

This invention is broadly applicable to any system in which a reactant fluid requires highly controlled introduction into another fluid. The contacting takes place by the circulation of the reactant in contact with a surface and the diffusion of the reactant fluid through the contact surface into contact with reactive fluid. The invention is most beneficial when the injected reactive fluid can also serve as an indirect heat exchange fluid.

The turbulence induced by the injection of the fluid into the film may be useful in the dispersion of the injected fluid throughout the fluid. As mentioned a corrugated plate may be another useful method of introducing turbulence for the distribution of the portion of the reaction and heat exchange liquid throughout the other liquid stream. The turbulence induced by the injection of the fluid as well as the optional corrugations can maintain mixing as the fluid flows to overcome laminar flow characteristics that give rise to temperature or concentration gradients. The turbulence induced by the injected fluid as well as any corrugations or turbulence inducing means will allow the dilute reaction to continue at high efficiency and with a dilute concentration of the reactive fluid over the entire height of the contacting surface.

A common example of a reaction suitable for the process and apparatus of this invention is in a sulfonation process which is meant to designate any procedure by which a sulfonic acid group with a corresponding salt or sulfonate halide is attached to a carbon atom. The sulfonation method for which this invention is most broadly suited is the treatment of an organic compound with a liquid phase sulfur trioxide. Common starting compounds for this sulfonation reaction include substrate materials such as alkyl olefins having 8-30 carbon atoms, alkyl benzenes having 8-15 carbon atoms, and aliphatic alcohols having 8-24 carbon atoms. A particularly preferred starting compound is toluene. The organic compounds enter the reaction channels in a liquid phase. Typical temperatures for substrate material in the reaction channels are in the range of 10-45° C. although actual temperatures may vary substantially with the organic material. The organic compounds may pass through the reaction channels in cross flow, countercurrent flow or concurrent flow with respect to the flow of the reactant through the distribution channels.

The invention is particularly useful for sulfonation reactions. Suitable sulfonating agents for the reactant stream include  $\text{SO}_3$ , sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and oleum ( $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ ),  $\text{SO}_3$  is the preferred sulfonating agent since it is essentially completely reacted to product and there is typically no need for downstream separation or recovery of the sulfonation reactant. Oleum and sulfuric acid on the other hand are not reacted to completion and will usually require a downstream separation stage for recovery when employed as the sulfonating agent.

The preferred  $\text{SO}_3$  reactant may be introduced into the reaction zone in combination with any suitable inert liquid, but is most advantageously added in a relatively pure form. One particular advantage of this invention is its suitability for introducing a relatively pure reactant stream into contact with the reactive stream. When using this invention for sulfonation, a reactive hydrocarbon stream may be sulfonated with an  $\text{SO}_3$  reactant at a 98% conversion on a once through passage of the reactive stream.

Another highly beneficial use of the reactor arrangement of this invention is in its use as an ethoxylation reactor. In such reactions, the material to be ethoxylated such as an alcohol or an alkylphenol flows through the reaction channels. Ethylene oxide is circulated as a liquid in a cocurrent or countercurrent direction. Close temperature control in such reactions is desired to prevent the formation of unwanted side products. The use of flat corrugations, the liquid injection and the heat exchange of this invention over a flat plate surface promotes liquid turbulence and overcomes the laminar nature of the flow which induces severe temperature and concentration gradients across the ethoxy-lated compounds.

The general operation of the contactor of this invention may be more fully appreciated from the drawings. FIG. 1 shows a generalized flow arrangement of a reaction zone 10 that injects a fluid reactant into another stream of reactive fluid and that provides simultaneous cooling by indirect heat exchange. FIG. 2 schematically shows a typical corrugated plate 18 having corrugations with peaks 52, valley 54, and perforations 50. Plates 18 define distribution channels 24 and reaction channels 14 as more fully shown in FIG. 3. Distribution channels 24 also serve as heat exchange channels in this particular arrangement and are equally well described as such. One liquid, a reactive fluid designated by stream B, enters the nozzle 32 at top of the reaction zone 10. Manifold 12 distributes the reactive fluid to the reaction channels 14 as shown in FIGS. 1 and 3. As shown by FIG. 3 the tops of the distribution channels 24 are closed to provide a sealed space for the isolated transfer of the additional reactant/heat exchange fluid.

The reactant fluid, shown by stream A in FIG. 3, enters the top of distribution channels 24 in reactor 10 through nozzles 22 and flows down the distribution channels 24. A desired amount the reactant fluid permeates through perforations 50 in plates 18 and diffuses into the reactive fluid as it exits from sides 20 of plates 18. The reactive fluid and reactant/heat exchange fluid will usually flow cocurrently. However, reactive stream and the reactant/heat exchange fluid may be introduced to the system for cocurrent flow as shown by stream A or cross-current flow as shown by stream C. The remaining volume of the reactant/heat exchange fluid exits the bottom of the distribution channels 24 through nozzles 26. After addition of any make-up fluid and heat exchange the heating or cooling, the reactant/heat exchange fluid returns for continued passage through channels 24 via nozzles 22 and 26. Suitable manifold arrangements for distributing and collecting the reactant fluid in any type of flow direction are well known.

Unreacted reactive fluid and products drop from reaction channels 24 and collect in lower chamber 28 at the bottom of reactor 10. Nozzle 30 withdraws fluid B from chamber 28 and passes it on to any necessary separation facilities for recovery of products and recycle of reactants.

A typical corrugation pattern for a plate 18 as shown in FIG. 2 may be uniform throughout or may vary down the length of the plate as shown in FIG. 2. FIG. 2 shows the corrugation patterns in the idealized fashion with solid lines showing the peaks 52 for the ridges of the corrugations and centralized valley portions 54 between the ridges.

Suitable distribution, heat exchange and contacting plates for this invention will comprise any plates which are easily secured in the reaction section in a stable configuration that readily retains a corrugated or other surface arrangement. The plates may be formed into curves or other configurations, but flat plates are generally preferred for stacking purposes. Thin plates are ordinarily used and typically have a thickness of from 1-2 millimeters. The plates are typically composed of ferrous or non-ferrous alloys such as stainless steels. The general herring bone pattern on the faces of the opposing corrugated plates preferably extends in opposite directions such that the opposing plate faces may be placed in contact with each other to form the flow channels and provide structural support to the plate sections.

The corrugation pattern may be varied to achieve a variety of contacting and reaction effects. In addition to increased turbulence such effects include heat exchange control. For example, where rapid heat exchange is desired, the corrugations may extend substantially longitudinally with respect to the fluid flow as shown by the upper section of corrugations in FIG. 2. As less cooling is needed, the ridges of the corrugations can be made more transverse, as shown by middle section 36 and lower section 38 in FIG. 2, to the flow to impede the flow thereby increasing surface area and heat turbulence for enhanced heat exchange. The reduced vertical run and increased pitch for each section of corrugation also increases the turbulence of the flowing liquid and improves the diffusion of the reactant fluid.

The transverse component of the ridges may increase continually or in the stepwise fashion as shown in FIG. 2 by sections 34, 36, and 38. As shown by FIG. 2, the channels defined by the corrugations generally run in a generally vertical direction. Chevron type corrugation arrangements that extend in a substantially horizontal direction should be avoided to prevent concentration of the liquid at the bottom points of the corrugation intersections. The arrangement of vertically continuous flow paths as shown in FIG. 2 keeps the fluid stream dispersed and avoids localized concentration of the fluid. A number of corrugated plate shapes can be used. Alternate pattern of corrugations are shown in FIG. 4 and FIG. 5.

The degree of turbulence may also be controlled by varying the amplitude of the corrugations and the frequency of the corrugations, which are otherwise referred to as the pitch and the depth of the corrugations. Corrugations having a large pitch or low frequency and shallow depth or low amplitude will provide a low degree of turbulence. Increasing either or both of the frequency and amplitude will raise the degree of turbulence.

The degree of heat transfer occurring over the heat transfer surface may be varied by including heat transfer plates between the permeable or perforated plates. In the case of corrugated plates, the provision of a separate heat transfer plate permits the pitch and number of corrugations on the heat transfer plate to vary independently with respect

to the corrugations on the perforated plates. Such an arrangement permits independent enhancement of heat transfer control over the length of the perforated plates without affecting the flow characteristic in the reaction channels. A heat exchange insert plate may be a flat plate with a turbulence inducing structure as shown in the U.S. Pat. No. 5,538,700, the contents of which are incorporated by reference herein, or an additional corrugated plate, preferably, containing perforations as shown by FIG. 2 and FIG. 5.

FIG. 4 depicts the tops of corrugated plates 44 and 46 into which corrugations are formed for defining distribution channels 58 and reaction channels 60. FIG. 4 shows the preferred arrangement where plates 44 and 46 are placed to contact adjacent corrugations in the distribution channels 58. The corrugations in the contacting channels 60 may be placed apart by distance D as shown in FIG. 4, but are preferably also placed in contact to avoid excessive deformation of the plates as a result of the relatively higher pressure in the distribution channels. The preferred arrangement of the corrugated plates with a herring bone pattern extending in different directions is more readily appreciated from FIG. 4. Corrugated plates 44 slope generally to the left as they extend downward while corrugated plates 46 extend transversely to the right as they slope downward.

The optional distance D will vary depending on the process conditions and the properties of the fluid. The distance D will typically be used merely to provide a larger volume in the flow channel for either the reactive or the reactant fluid. Spacing D may be maintained by use of occasional spacers that contact the points of the corrugations. Such spacers may consist of thin pins that extend over the entire vertical length of the contacting channels or thin bars that extend transversely across the contacting channels.

As more clearly illustrated in FIG. 6, all of the plates 61 defining the contacting channels 62 and the distribution channels 64 will preferably contain perforations except the outermost plates 69 defining the outermost channels 66. The outermost channels are preferably distribution and heat exchange channels so that all of the contacting channels receive heat exchange.

#### ILLUSTRATIVE EMBODIMENT

This invention can be used to operate an isothermal sulfonation process for the sulfonation of an alkyl benzene with sulfur trioxide. In such an arrangement, an alkyl benzene stream comprising substituted benzene with alkyl groups and having from 12-14 carbon atoms passes in liquid phase through reaction channels as depicted in FIG. 1 and FIG. 3. A liquid stream of  $\text{SO}_3$  flows parallel to the alkyl benzene through the distribution channels to provide the sulfonating agent. Approximately 5% of the liquid  $\text{SO}_3$  stream flows across the perforated plate separating the distribution and reaction channels and through fine perforations having an average diameter of about 0.02 in. that provide an opening area of about 5% of the total area of each plate. The temperature of the liquid  $\text{SO}_3$  containing stream entering the distribution channels is about 20-25° C. The reactant stream passes through the reaction channel at a mass flow rate of about 500 Kg/Hr. The reactant stream as it passes over the plates is maintained at a temperature of about 50° C. by the excess  $\text{SO}_3$  reactant that passes through

the distribution/heat exchange channels. A once through passage of the hydrocarbon stream will produce an approximately 98% conversion.

What is claimed is:

1. A process for the reaction of a fluid stream by the controlled addition of a liquid reactant, said process comprising:
  - passing a first stream comprising a reactive fluid into a plurality of reaction channels defined by a first side of a plurality of stacked plates;
  - circulating a second stream comprising a reactant fluid through a plurality of distribution channels defined by a second side of said plurality of plates to provide indirect heat exchange with the reactive stream;
  - distributing a portion of said reactant fluid through permeable portions distributed over the surface of said plates to control the contact of said reactive fluid with the reactant fluid; and,
  - recovering a reaction product from the reaction channels.
2. The process of claim 1 wherein the reaction is the sulfonation of a substrate with sulfur trioxide.
3. The process of claim 1 wherein said plates are corrugated and stacked to define vertically extended channels.
4. The process of claim 3 wherein said corrugations run at least partially transverse to the flow of the reactant stream.
5. The process of claim 4 wherein said corrugations extend diagonally across the surface of the plates in a plurality of rows and the vertical length of each diagonal is less than the vertical height of the plates.
6. The process of claim 4 wherein the corrugations of adjacent plates are in contact.
7. The process of claim 1 wherein said plates are perforated to provide said permeable sections.
8. The process of claim 1 wherein either the amplitude or the frequency of the corrugations is established to induce a desired degree of turbulence into said reactant stream as it passes down said corrugated surface.
9. The process of claim 1 wherein the volume of said reactant fluid passing into said reaction channels is less than 5% of said volume of said reactant fluid entering the distribution channels.
10. The process of claim 1 wherein the reactant fluid and the reactive fluid are maintained in liquid phase.
11. A process for the sulfonation of an organic liquid with a sulfonating liquid, said process comprising:
  - passing a reactive organic liquid through reaction channels defined by a first side of a plurality of vertically positioned corrugated plates that contain perforations;
  - circulating a reactant stream containing  $\text{SO}_3$  through distribution channels defined by the second side of said vertical positioned plates to indirectly exchange heat with said organic liquid;
  - distributing a portion of the reactant stream through the perforations, and contacting the reactant stream with the organic liquid in said reaction channels; and,
  - recovering a reaction product from said reaction channels.
12. The process of claim 11 wherein said organic liquid comprises toluene.

\* \* \* \* \*



US006228341B1

(12) **United States Patent**  
Hebert et al.(10) **Patent No.:** US 6,228,341 B1(45) **Date of Patent:** May 8, 2001(54) **PROCESS USING PLATE ARRANGEMENT  
FOR EXOTHERMIC REACTIONS**(75) **Inventors:** Philippe Hebert, Hoffman Estates;  
Jacques J. L. Romatier, Riverwoods;  
Peter R. Pujado, Kildeer; Bipin V.  
Vora, Darien, all of IL (US)(73) **Assignee:** UOP LLC, Des Plaines, IL (US)(\*) **Notice:** Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.(21) **Appl. No.:** 09/149,606(22) **Filed:** Sep. 8, 1998(51) **Int. Cl.<sup>7</sup>** ..... C01C 1/04(52) **U.S. Cl.** ..... 423/352; 423/360; 423/361(58) **Field of Search** ..... 423/352, 360,  
423/361(56) **References Cited**

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Paschall

(57)

## ABSTRACT

A process and apparatus cools a heat exchange type reaction zone by passing the incoming reactants through heat exchange channels in heat exchange relationship with the reaction zone. The invention simplifies the operation and construction of the heat exchanging type reaction zone by directly communicating reaction channels that contain the reaction with the heating channels that heat reactant across an open manifold located at the end of the channels. Additional reactants, cooling fluids, or other diluents may enter the process directly through the manifold space to permit further temperature control of the reaction zone. The invention promotes better heat transfer efficiency than tube and shell heat transfer arrangements that have been used for similar purposes. The narrow channels are preferably defined by corrugated plates. The reaction channels will contain a catalyst for the promotion of the primary reaction.

16 Claims, 6 Drawing Sheets

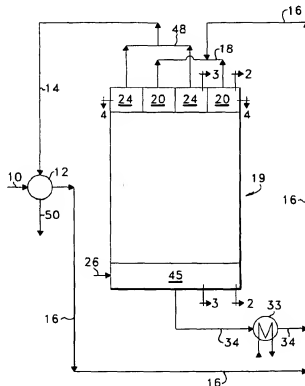
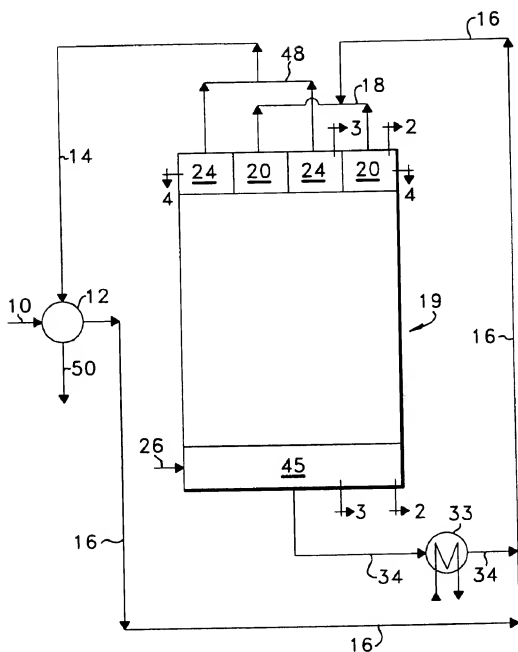




FIG. 1



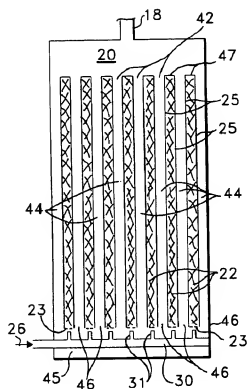


FIG. 2

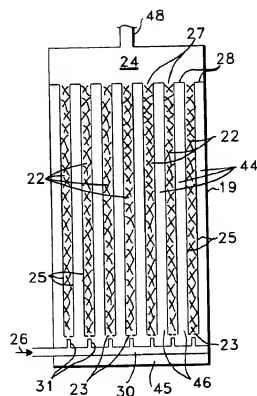


FIG. 3

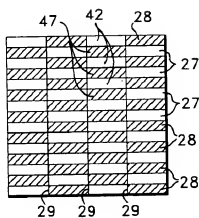


FIG. 4

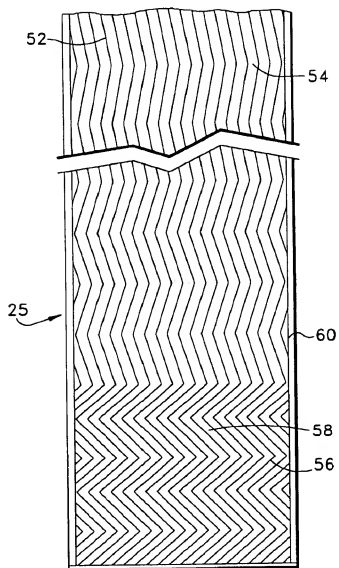


FIG. 5

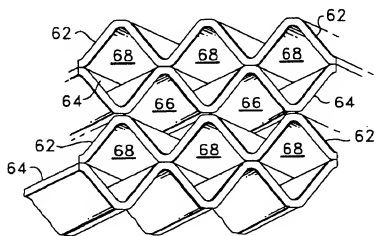


FIG. 6

FIG. 7

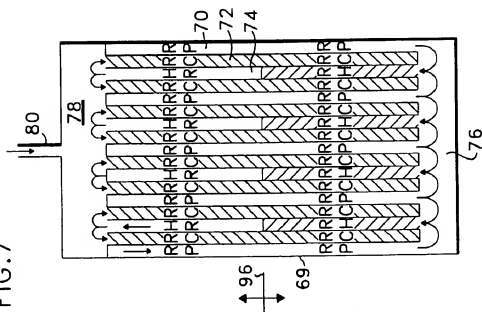


FIG. 8

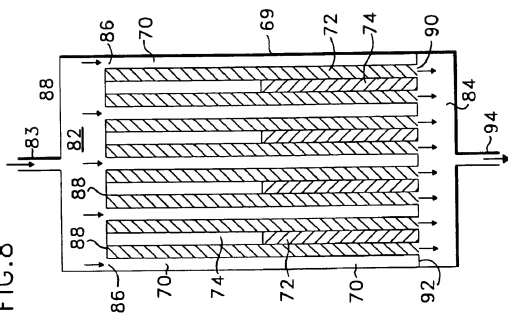
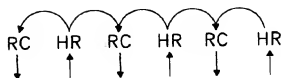
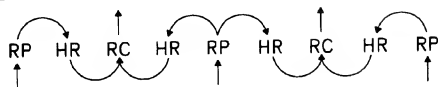


FIG. 9

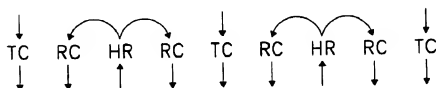
CASE 1



CASE 2



CASE 3



CASE 4

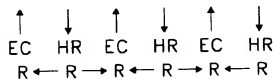
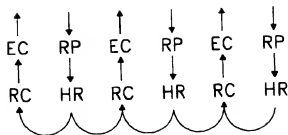
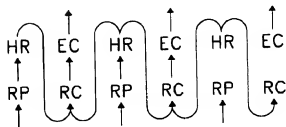


FIG. 10

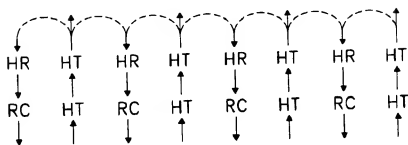
CASE 5



CASE 6



CASE 7



1

## PROCESS USING PLATE ARRANGEMENT FOR EXOTHERMIC REACTIONS

### FIELD OF THE INVENTION

This invention relates generally to plate type exchangers for cooling a reaction zone by indirect heat exchange with a cooling fluid stream.

### BACKGROUND OF THE INVENTION

In many industries, like the petrochemical and chemical industries, contact of reaction fluids with a catalyst in a reactor under suitable temperature and pressure conditions effects a reaction between the components of one or more reactants in the fluids. Most of these reactions generate or absorb heat to various extents and are, therefore, exothermic or endothermic. The heating or chilling effects associated with exothermic or endothermic reactions can positively or negatively affect the operation of the reaction zone. The negative effects can include among other things: poor product production, deactivation of the catalyst, production of unwanted by-products and, in extreme cases, damage to the reaction vessel and associated piping. More typically, the undesired effects associated with temperature changes will reduce the selectivity or yield of products from the reaction zone. The heating or chilling effects may be useful for a variety of exothermic and endothermic processes. Dehydrogenation processes represent one class of endothermic processes that particularly benefit from indirect reaction zone heating to maintain a desired temperature profile.

This invention is particularly suited for exothermic processes. Exothermic reaction processes encompass a wide variety of feedstocks and products. Moderately exothermic processes include methanol synthesis, ammonia synthesis, and the conversion of methanol to olefins, phthalic anhydride manufacture by naphthalene orthoxylyene oxidation, acrylonitrile production from propane or propylene, acrylic acid synthesis from acrolein, conversion of n-butane to maleic anhydride, the production of acetic acid by methanol carbonylation and methanol conversion to formaldehyde. Oxidation reactions generally represent a class of highly exothermic reactions. The exothermic nature of these reactions has led to many of these reactions incorporating a cooling system into the reactor design. Those skilled in the art routinely overcome the exothermic heat production with quench or heat exchange arrangements. Extensive teachings detail methods of indirectly exchanging heat between the reaction zone and a cooling medium. The art currently relies heavily on tube arrangements to contain the reaction and supply indirect contact with the cooling medium. The geometry of tubular reactors poses layout constraints that require large reactors and vast tube surface to achieve high heat transfer efficiencies.

Other process applications accomplish indirect heat exchange with thin plates that define channels. The channels alternately retain catalyst and reactants in one set of channels and a heat transfer fluid in adjacent channels for indirectly heating or cooling the reactants and catalysts. Heat exchange plates in these indirect heat exchange reactors can be flat or curved and may have surface variations such as corrugations to increase heat transfer between the heat transfer fluids and the reactants and catalysts. Many hydrocarbon conversion processes will operate more advantageously by maintaining a temperature profile that differs from that created by the heat of reaction. In many reactions, the most beneficial temperature profile will be obtained by maintaining substantially isothermal conditions. In some

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cases, a temperature profile directionally opposite to the temperature changes associated with the heat of reaction will provide the most beneficial conditions. For such reasons it is generally known to contact reactants with a heat exchange medium in cross flow, cocurrent flow, or countercurrent flow arrangements. A specific arrangement for heat transfer and reactant channels that offers more complete temperature control can be found in U.S. Pat. No. 5,525,311; the contents of which are hereby incorporated by reference. Other useful plate arrangements for indirect heat transfer are disclosed in U.S. Pat. No. 5,130,106 and U.S. Pat. No. 5,405,586.

Isolating reactants from coolants at the inlets and outlets of a plate exchanger arrangement leads to elaborate designs and intricate manufacturing procedures. Simplification of the fluid transfer at the inlets and outlets of a plate exchanger arrangement improves the cost effectiveness of and practicality of such arrangements in many processes.

It is, therefore, an object of this invention to simplify plate exchanger arrangements for the cooling of an exothermic reaction zone by indirect heat transfer.

It is a further object of this invention to simplify the feed and recovery of reactants and coolants from a heat exchange reactor using narrow channels.

### BRIEF SUMMARY OF THE INVENTION

This invention incorporates open chamber portions to transfer fluid for indirectly transferring heat produced in the reaction channels to the heated channels that absorb heat by raising the temperature of a reactant-containing stream. A chamber communicates the ends of the channels to provide simple transfer of the heated channels with the reaction zone across common ends of the narrow channels. The chamber permits additional temperature control by the addition or removal of reactants and by cooling fluids or other streams at an intermediate point along the total channel flow path. Insertion of additional chambers along the flow path of either the reaction or heated channels provides locations for more temperature adjustment and control.

Suitable channel arrangements may exchange heat directly across a common heat exchange surface or may use an intermediate heat transfer fluid to transfer heat from the cooling zone to the reaction zone while simultaneously providing temperature adjustment control. One arrangement of the intermediate heat transfer fluid may place the cooling zone and the reaction zone at different portions of common channels and may pass the intermediate fluid through adjacent channels to transfer heat out of reaction channels at one location and transfer heat back into the heated channels at a downstream channel location. In other arrangements the intermediate channels and the reaction channel may lie in a parallel arrangement between the heated channels to adjust the temperature in the reaction channels through the heated channels.

In most cases the reactant-containing stream will pass through the heated channels and then directly into the reaction channels to provide continuous fluid flow through all channels with an essentially constant pressure in all of the channels. Circulation of the reactant-containing stream around the outer shell of the vessel that contains the channel defining plates can offer further temperature control. Appropriate processes may also incorporate an endothermic reaction into the heated channels to further control temperatures.

The resulting reaction apparatus designed in accordance with this invention offers flexibility in temperature control with a relatively simple plate reactor arrangement. The outer containment vessel can completely support the plate

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arrangement from either its top or its bottom. Direct passage of heated reactants from the heated channels to the reaction channel from common ends in a chamber eliminates welding at least one end of multiple thin plates.

The presence of narrow heat exchange channels for cooling the reaction zone and for heating the reactants constitutes an essential requirement of this invention. With respect to fluid flow through the reaction channels and heated channels, the fluids may have cocurrent flow or cross flow with respect to some of the channels. However, advantageous use of the chamber design of this invention requires that at least two adjacent sets of channels establish countercurrent flow.

Variations in the catalyst loading within the reaction channels and the addition of catalyst for endothermic reactions may satisfy different processing objectives. For example, short loading of catalyst in reaction channels can provide a space above or below the reaction zone for additional feed preheat or effluent cooling. Again, extending the heated channels can provide additional surface area for open channel heat exchange against the exiting reaction zone effluent or the incoming reactants.

Another variation on the plate arrangement can use two or more separate stacks of heat exchange plates or "reaction stacks" to conduct different reactions and heat exchange steps in isolated reaction zones. For example, one arrangement of alternating narrow channels in a reaction stack may contain catalyst for one reaction step in one set of channels while exchanging heat with the entering feed in another set of channels. A system of manifolds can then pass the isolated preheated feed and secondary stream reforming effluent to another section of heat exchange channels that again indirectly contacts the hot gases from the secondary reforming reaction in indirect heat exchange with channels containing catalyst for a primary reforming reaction. Suitable ducting can then return all or any portion of the primary reforming reaction zone effluent to the secondary reforming reaction zone. Integration of the manifolds with external pipes can further enhance process control.

The plates defining the channels for containing the reactions and heat exchange gases may have any configuration that produces narrow channels. A preferred form of the heat exchange elements is relatively flat plates having corrugations defined therein. The corrugations serve to maintain spacing between the plates while also supporting the plates to provide a well supported system of narrow channels. Additional details on the arrangement of such plate systems are shown in U.S. Pat. No. 5,525,311; the contents of which are hereby incorporated by reference.

Suitable plate arrangements may also incorporate perforated plates. Most advantageously, perforated plates would allow the controlled quantities of the heated reactant to flow directly into the reaction channels. Perforated plates would disperse the introduction of the reactant over a desired portion of the reaction zone. Those skilled in the art will recognize other variations in plate configurations that can provide additional benefits to the integrated reforming stages.

Accordingly, in a broad process embodiment this invention contacts reactants with a catalyst in a reaction zone while indirectly heating or cooling the reactants in the reaction zone by indirect heat exchange. The process passes an input stream containing at least a portion of a fluid for the reaction zone through a plurality of narrow heat exchange channels defined by at least a first portion of spaced apart plates to heat or cool the input stream and supply a portion

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of the fluid entering the reaction zone. The input stream may comprise a reactant or an inert stream that passes through the reaction zone. The heated or cooled input stream passes with or without additional fluid input, to the reaction zone as a reaction stream that contacts a catalyst material in the reaction zone to produce a reacted stream. The input stream undergoes heat exchange in the heat exchange channels by indirect heat exchange with the reaction stream or the reacted stream across the spaced apart plates. A common manifold communicates common ends of the at least two channels defined by the spaced apart plates to indirectly exchange heat from the reaction zone to the heat exchange channels. The process collects at least a portion of the reacted stream downstream of channels defined by a second portion of the spaced apart plates. In a specific aspect of this embodiment the common manifold communicates the outlet of the heat exchange channels with the inlets of the reaction channels and preferably an additional stream enters the manifold for admixture with input stream as it exits the heat exchange channels.

In a more specific form of this embodiment, the process passes the reactant-containing stream through a plurality of narrow heated channels defined on one side of spaced apart plates and a plurality of narrow reaction channels defined by the opposite side of the spaced apart plates. Another specific operation communicates common ends of the heated channels and the reaction channels across an open chamber at one of the reaction and heated channels to pass at least a portion of the reactant containing stream from the heated channels to the reaction channels as at least a portion of the heated reaction stream.

Accordingly, in a more narrow process embodiment this invention contacts reactants with a catalyst in a reaction zone while indirectly heating the reactants and cooling the reaction zone by indirect heat exchange. The process passes a reactant containing stream through a plurality of narrow heated channels defined by at least a first portion of spaced apart plates to heat the reactant-containing stream and to produce a heated reactant stream. The heated reactant stream passes as a reaction stream to a reaction zone that contacts the reaction stream with a catalyst material in the reaction zone to produce a reacted stream. The reactant-containing stream undergoes heating from the reacted stream in the heated channels by indirect heat exchange with the reaction stream or the reacted stream across the spaced apart plates. A common manifold communicates common ends of at least two channels defined by the spaced apart plates to indirectly exchange heat from the reaction zone to the heated channels. The process collects at least a portion of the reacted stream downstream of channels defined by a second portion of the spaced apart plates.

In a more specific form of this embodiment the process passes the reactant-containing stream through a plurality of narrow heated channels defined on one side of spaced apart plates and a plurality of narrow reaction channels defined by the opposite side of the spaced apart plates. Another specific operation communicates common ends of the heated channels and the reaction channels across an open chamber at the one end of the reaction and heated channels to indirectly exchange heat from the reaction zone to the heated channels to the reaction channels as at least a portion of the heated reaction stream.

In an apparatus embodiment this invention includes a plurality of reaction channels defined by a plurality of spaced apart plates having heated reactant inlets at one end of the reaction channels and reacted stream outlets at an opposite end of the reaction channels. The reaction channels



contain means for retaining a solid catalyst in the reaction channels. A plurality of heated channels defined by a plurality of spaced apart plates in an indirect heat exchange relationship with the reaction channels has cold reactant fluid inlets at one end and heated reactant outlets at an opposite end. A containment vessel houses the plurality of spaced apart plates. The containment vessel defines a chamber for communicating the heated reactant outlets with the heated reactant inlets. The containment vessel includes a support structure for supporting one end of the plates from the top or the bottom of the containment vessel.

Additional embodiments, arrangements, and details of this invention are disclosed in the following detailed description of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow diagram of a reactor and heat exchanger arrangement for a reactor arranged in accordance with this invention.

FIG. 2 is a section of the schematic heat exchange reactor shown in FIG. 1 taken at section 2—2.

FIG. 3 is a section of the schematic heat exchange reactor shown in FIG. 1 taken at section 3—3.

FIG. 4 is a horizontal section of the schematic heat exchange reactor shown in FIG. 1 taken at section 4—4.

FIG. 5 is a schematic drawing of a flat plate element showing a corrugation pattern.

FIG. 6 is an isometric view of corrugated plates forming flow channels.

FIGS. 7 and 8 are schematic diagrams of alternate arrangements for the heating and reaction channels arranged in accordance with this invention.

FIGS. 9 and 10 are charts showing the placement of heat exchange and reaction zones in channels.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention may be useful in any exothermic or endothermic process. This invention is particularly useful in any exothermic process where a reactant or a portion of a reactant provides a heat sink for cooling an exothermic reaction in an arrangement of plate exchanger elements. Additional requirements of this process for compatibility with a plate exchanger arrangement will typically require that there be a relatively low  $\Delta T$  between the exothermic and endothermic reaction zones. Differential temperatures of 200° C. or less are preferred for this invention. Due to the interconnection of adjacent channels differential pressures will remain low and will typically reflect pressure drop requirements through the catalyst bed. Ordinarily the differential pressure across plate elements will not exceed 0.5 MPa.

The reaction channels will contain a catalyst for promoting the exothermic reaction process. Suitable catalysts for the previously mentioned exothermic processes as well as other exothermic or endothermic process applications are well known to those skilled in the art. Catalyst in a particulate form may fill the reaction channels in an amount that provides the desired reaction time and any pre-reaction heating or post-reaction cooling in the reaction channels. As an alternate to a particulate catalyst, the catalyst may also be coated on the surface of the plates in the various reforming zones. It may be particularly advantageous to coat the reaction catalyst onto the plates to provide an upper catalytic section and a lower catalyst-free section that are maintained

in a heat exchange relationship with a catalytic secondary reforming section on the other side of the plates.

Where suitable for balancing heat requirements of a particular reaction, those skilled in the art are aware of particular catalysts for promoting complementary endothermic reactions. Such catalysts may advantageously reside in the heating channels to provide reactive cooling as well as cooling from sensible or latent heat of the reactants. An example of such an endothermic and exothermic catalyst combination is steam reforming. Such an arrangement is particularly suited for incorporation into a multiple pass channel arrangement that interconnects only two pairs of adjacent channels and places an exothermic reaction channel between alternate heating channels and endothermic reaction channels. In a three pass arrangement of such a configuration, the relatively cold reactants flow into the heating channels where indirect heat exchange with the reaction channels provides the respective heating and cooling. Flowing the reacted stream from the exothermic reaction channels into the endothermic reaction channels provides additional cooling to the reaction channels across the shared plates that define the endothermic reaction channel as well as the adjacent exothermic reaction channels.

FIG. 1 illustrates a basic flow arrangement for the process of this invention. The discussion of FIG. 1 uses the production of phthalic anhydride (PA) as an example of a specific context for an exothermic process. However, the general principles apply to any exothermic process including those previously enumerated. Looking then at FIG. 1, in a basic flow arrangement of this invention a relatively cold stream comprising orthoxylene and oxygen or air enters the process via line 10. In the case of air the feed proportions are generally in a range of from 40 to 300 g oxygen per Nm<sup>3</sup> of air and preferably the proportion of oxygen to air will not exceed 200 g per Nm<sup>3</sup> of air. The entering feed undergoes heat exchange in a conventional heat exchanger 12 with a PA gas product stream carried by a line 14. The preheated feedstream passes via line 16 to a distribution header 18. Distribution header 18 supplies the heated feed to distribution spaces 20 in a heat exchanger reactor 19. As further shown by FIG. 2, distribution space 20 distributes the heated synthesis gas to the top of a plurality of inlets 42 of heated channels 44. Distribution space 20 has the tops 47 of reaction channels 22 closed to gas flow to prevent the incoming reactants from flowing directly into contact with the PA oxidation catalyst contained therein. Downward passage of the feed through channels 44 heats the feed gases while simultaneously cooling reaction channels 22 across the large surface area provided by the plates 25 that define the heating and reaction channels. Manifold space 45 collects the heated orthoxylene-containing feed from the open outlets 46 of heated channels 44.

As shown in FIGS. 2 and 3, manifold space 45 redistributes and collects feed from channels 44 to the inlets 23 of reaction channels 22. The heated oxidation reactants pass through the channels 22. Reaction channels 22 contain the above mentioned catalyst material that promotes the oxidation of the orthoxylene. Suitable catalyst materials comprise a variety of vanadium phosphates. The catalyst material may reside in the channels as a coating applied to plates 25 or as discrete particles. The inlets 23 of the reaction channels 22 are open to gas flow. Where the catalyst material comprises particulate material, a screen material located across inlets 23 prevents catalyst from falling from channels 22. FIGS. 1 and 3 depict a collection space 24 that collects the effluent from the primary reforming zone across the open tops that provide outlets 27 of channels 22. A manifold 48 gathers the

collected PA-containing effluent and transfers it into product line 14 for recovery downstream of exchanger 12 via line 50.

The arrangement of distribution space 20 and collection space 24 to selectively distribute the entering reactants and collect the oxidation zone effluent is more fully appreciated from FIG. 4. As shown by FIG. 4, those portions of reaction channels 22 that coincide with collection space 24 maintain outlets 27 open for free communication therewith. Conversely, those portions of heated channels 44 that coincide with collection space 24 have a closure 28 that prevents fluid communication with collection space 24. Distribution space 20 has the reverse relationship to channels 22 and 44 wherein coinciding portions of channels 44 communicate openly across inlets 42 while coinciding portions of channels 22 are blocked from communication with distribution space 20 by closures 47. FIG. 4 also shows the partitions 29 that internally segregate collection spaces 24 from distribution spaces 20.

Manifold space 45 may provide additional temperature and reaction functions or controls. For example, intermediate nozzles 31 may withdraw or add fluid to manifold space 45. Withdrawal of fluid may provide additional cooling by passing a portion of the withdrawn reactant-containing stream through a cooler via a line 34 and by recirculating the cooled fluid to heated channels 44 via line 16, header 18, and distribution space 20. It is also not necessary to the practice of this invention that each reaction channel be alternated with a heated channel. Possible configurations of the reaction section may place two or more heat exchange channels between each reactant channel to reduce the pressure drop on the heat exchange medium side, particularly when recirculating a portion of the reactant stream for additional cooling. When used for this purpose, a plate separating adjacent heat exchange channels may contain perforations. Providing an increased flow area of heated channels relative to the reaction channels will accommodate recirculation of a portion of the reactant containing stream without excessive pressure drop. The use of packing or perforated plates within the heated channel can enhance heat transfer with the reaction channels while providing good circulation over the entire cross section of the heated channel.

As a further example of additional functions, a line 26 may transfer additional fluids into the manifold space 45. A distributor, feasibly in the form of a pipe 30, may use nozzles 31 to inject the additional fluid at a location near inlets 23 of reaction channels 22. Injection near the inlets 23 concentrates the entry of the added fluid directly into channels 22. Injected fluids may include additional reactants, supplemental cooling fluid, or other diluents.

In general, the invention relies on relatively narrow channels to provide the efficient heat exchange across the thin plates. The channel width should be less than one inch on average with an average width of less than  $\frac{1}{2}$  inch preferred. Suitable plates for this invention will comprise any plates that allow a high heat transfer rate. Thin plates are preferred and usually have a thickness of from 1 to 2 mm. The plates are typically composed of ferrous or non-ferrous alloys such as stainless steel. Preferred alloys for the plates will withstand extreme temperatures and contain high proportions of nickel and chrome. The plates may be formed into curves or other configurations, but flat plates are generally preferred for stacking purposes. Again, each plate may be smooth and additional elements such as spacers or punched tabs may provide fluid turbulence in the channels.

Preferably, each plate has corrugations that are inclined to the flow of reactants and heat exchange fluid. The corruga-

tions maintain a varied channel width defined by the height of the corrugations. In the case of corrugations, the average channel width is most practically defined as the volume of the channels per the cross-sectional area parallel to the primary plane of the plates. By this definition, corrugated plates with essentially straight sloping side walls will have an average width that equals half of the maximum width across the channels.

FIG. 5 shows the preferred corrugation arrangement for the plates 25 that divide the central portion of heat exchange reactor 19 into heated channels and reaction channels. The corrugation pattern can serve at least two functions. One function is to structurally support adjacent plates. The other function is to promote turbulence for enhancing heat exchange efficiency in the narrow reaction channel. FIG. 5 shows corrugations defined by ridges 52 and valleys 54. The frequency or pitch of the corrugations may be varied as desired to promote any varying degree of turbulence. Therefore, more shallow corrugations with respect to the fluid flow direction, as shown by ridges 52 and valleys 54, will produce less turbulence, and whereas a greater corrugation pitch with respect to the direction of fluid flow, as shown by ridges 56 and valleys 58, will provide increased turbulence where desired. The pitch of the corrugations and the frequency may also be varied over a single heat exchange channel to vary the heat transfer factor in different portions of the channel. Preferably, the channels may contain a flat portion 60 about their periphery to facilitate closure of the channels about the sides and tops where desired.

FIG. 6 shows a typical cross-section of a corrugated plate arrangement wherein the corrugations of plates 62 extend in an opposite direction to the corrugations of plates 64 thereby defining alternate reaction channels 66 and heated channels 68. FIG. 6 illustrates the preferred arrangement of corrugated plates where the herring bone pattern on the faces of opposing corrugated plates extends in opposite directions and the opposing plate faces contact each other to form the flow channels and to provide structural support to the plate sections.

Additional channels defined by the plates can provide a variety of supplementary functions. In addition to channels for the heating of reactants and cooling of the reaction zone that contains the exothermic reaction, other channel functions may include additional preheating of the feed for the exothermic reaction zone, cooling of the effluent from the exothermic reaction zone, and retaining a catalyst for an endothermic reaction.

A reactor arrangement 69 having multi-function channels is shown in FIGS. 7 and 8. FIG. 7 shows one such channel arrangement with the functions of the different channels coded in the schematic representation. The coding terminology generally refers to the internal component or function of the channels and/or the effect of that function on the component within the subject channel. The letters "RP" designate a channel or channel section for preheating reactants. "HR" designates a channel or channel section that heats the reactants for the exothermic reaction. The letters "RC" indicate a channel or channel section that contains an exothermic reaction and reaction catalyst that receives indirect cooling. Letters "RH" show a channel or portion of a channel in which reactant heating takes place to confine an endothermic reaction which further cools the exothermic reaction zone or its reactants.

#### EXAMPLE

To more fully illustrate the process and apparatus of this invention, the following example shows the calculated

operation of a process steam reforming of methane to produce methanol in a plate channel reactor arrangement of the type depicted by FIGS. 7 and 8. A methane-steam reforming process provides a mix of exothermic and endothermic reactions suitable for use in the arrangement as shown. Looking then at FIGS. 7 and 8 in the context of the steam reforming process, flow through the channels for the exothermic and endothermic process steps requires two different collection and distribution space arrangements. Fluid flow through the distribution/collection spaces can be controlled in a manner analogous to that described and depicted in FIGS. 1-4. In this example, 100 g moles of a methane feed and 250 g of steam enter the process. 60 g moles of the methane representing all of the methane feed for the endothermic reaction zone enters the plate reactor arrangement 69 through a nozzle 83. The amount of feed is targeted to provide a hydrogen to carbon ratio in the product of 2:1. A feed distribution that provides a manifold that distributes the feed to inlet 86 of the preheat channels 70. Closure plates 88 block the tops of channels 72 and 74 where the channels are contiguous with the distribution chamber 82. Feed to the exothermic and endothermic reaction zones passes through the feed preheat channels 70 where indirect heat exchange with the exothermic reaction zone channels 72 raises the temperature of the feed. Preheated feed from channels 70 flows into a manifold space 76 shown in FIG. 7. Manifold space 76 serves as a collection and distribution space that forms a part of reactor 69. Manifold space 76 communicates the preheated feed with a lower section of channels 74 that contain catalyst for reactive cooling of the reactants from the preheat channels as a result of the endothermic reaction.

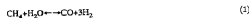
In this example of steam reforming, the lower section of channels 74 provides a space for the primary reforming reaction which produces synthesis gas from a fluid hydrocarbon such as natural gas. Operating conditions in the primary reforming stage can be in a temperature range of from 420 to 920° C. and, in this example, operate in a range of from 800 to 870° C. The specific operating pressures employed are principally influenced by the pressure requirements of the subsequent processing operations in which the reformed gas mixture is employed. Any super atmospheric pressure can normally be used in the practice of most reforming operations and is suitable for most applications of the apparatus and process of this invention. Pressures of from about 2 to 5 MPa are commonly employed although lower pressures can be used and pressures as high as 10 MPa can be maintained in particular applications. In this example the primary reaction section operates at a pressure of about 3.8 MPa.

This endothermic reaction will contain a suitable catalyst composition such as solid catalyst granules deposited on an inert carrier material. The reactant stream normally contains particulate catalyst in the endothermic and exothermic reaction channels of the steam reforming process. This steam reforming process can use one or more suitable reforming catalysts employed in conventional steam and secondary reforming operations. The metals of Group VIII of the Periodic System and/or oxides thereof and metals of the left hand elements of Group VI and/or oxides thereof are known reforming catalysts. Specific examples of reforming catalysts that can be used are nickel, nickel oxide, cobalt oxide, chromia, molybdenum oxide, and rhodium based catalyst on an  $\alpha$ -alumina support. The catalyst can be employed with promoters and can receive various special treatments known in the art for enhancing its properties. Promoted nickel oxide catalysts are generally preferred, and the primary reformer

channels are packed with solid catalyst granules, usually comprising metals such as nickel or other catalytic agents deposited on a suitable inert carrier material.

The catalyst may comprise discrete particles usually in a size range of from 2 to 15 mm in diameter. The particles may have any shape, but they will typically comprise spheres or cylinders. The secondary reforming zone commonly contains a bed of similar catalyst material. As an alternate to a particulate catalyst, the catalyst may also be coated on the surface of the plates in the various reforming zones as previously mentioned.

In this example the primary feed contacts particles of a Nickel type catalyst at a GHSV of 5000-8000  $\text{h}^{-1}$ . The primary reaction converts the heated feed to a gas mixture containing principally hydrogen and carbon monoxide according to reaction (1) as follows:



The preheated feed travels upwardly through the primary reforming channels 74 passing through the catalytic section "RH" and a non-catalytic section. The non-catalytic section "HR" provides further heating of the reactants while simultaneously cooling channels "RC" before entering a manifold space 78. Additional reactants or cooling fluids may enter space 78. The manifold space 78 through nozzle 80. In this case an oxygen-containing gas and, optionally, additional feed or combustion fuel, enter manifold space 78 through nozzle 80. Manifold space 78 again serves as a collection and distribution space that forms a part of reactor 69. Partitions similar to those shown as 29 in FIGS. 1-4 separate manifold space 78 from the manifold space of chamber 82. Manifold space 78 mixes any fluid entering via nozzle 80 with the primary reforming zone effluent before distributing the heated feed to the secondary reforming channels 72. In this example, an additional 40 g moles of methane feed and 35 g moles of oxygen enter the secondary reforming channels.

The secondary reforming channels 72 contact the entering feed with nickel based catalyst at an average temperature of 1065° C. and pressure of 3.8 MPa, along their entire length to promote the exothermic secondary reforming reaction. As the mixture passes downwardly through secondary reforming channels 72, it heats the channels 74 containing the primary reactants as well as the feed preheat channels 70. The necessary heat is supplied by the conventional secondary reforming reaction that oxidizes a fluid hydrocarbon fuel such as a side stream from the fluid hydrocarbon feedstream or a portion of the primary reforming effluent stream. Oxidation supplies the heat to the primary reformer by indirect heat exchange from channels RC. In the practice of the invention and in conventional practice, the secondary reforming operation is carried out to react unconverted methane present in the primary reformer effluent with air or other oxygen-containing gases. The following reactions occur in the secondary reforming zone:



Reactions (2), (3), and (4) are exothermic reactions that tend to occur quite rapidly in the secondary reaction space. As the

resulting gas mixture passes through the catalyst bed of the secondary reformer zone, the remaining methane is converted by reaction with steam in accordance with reaction (1) above and by the reaction with oxygen according to reaction (3) above so that very little methane remains in the product gas of the process. The strongly endothermic reaction (1) is a relatively slow reaction that occurs throughout the passage of the gases through the catalyst bed of the secondary reforming zone, thereby cooling the gases from the high temperatures reached by reactions (2), (3), and (4) that occur toward the feed end of the secondary reaction zone. In the practice of the invention, the proportions of oxygen and of the fluid hydrocarbon feed passed to the integrated primary-secondary reformers maintain an essentially, or completely, autothermal process with essentially no fuel requirement. An advantageous feature of the invention is the flexibility of being able to by-pass a portion of the hydrocarbon feedstream directly to the secondary reforming reaction space at the feed end of the secondary reforming zone.

FIG. 8 shows an additional collection space 84 that forms a part of reactor 69 and again uses partitions to separate it from manifold space 76. The effluent from the exothermic reaction-containing channels enters collection space 84 and the open bottoms that provide outlets 90 of the secondary reforming channel 72. Outlets 90 contain an appropriate screen material to retain catalyst in the secondary reforming channels while permitting fluid to exit from the channels. The bottoms of primary reforming channels 74 use closure plates 92 where they pass across collection space 84. A secondary reforming nozzle 94 withdraws the collected secondary reforming effluent. Further by-passing of feed between the primary and secondary reforming zone may be accomplished by external piping that communicates distribution space 82, collection space 84, and manifold spaces 76 with interconnecting flow paths. After passing through the two reaction steps, the process produces 54.3 g moles of a product having a H/HIC ratio of 2.21.

The reaction arrangement has the versatility to offer additional preheating as well as isolation of the exothermic reaction zones. This is readily accomplished by varying the location of the catalyst loading between channels. Optionally, the space at one end of a channel may be used as a feed preheating zone or as an effluent cooling zone. FIGS. 7 and 8 schematically illustrate a partial loading of catalyst in the channels by a catalyst level line 96. Primary reforming channels 74 may contain catalyst from below line 96 to the inlets of the channels 74. In such an arrangement for steam reforming, as feed flows downwardly through feed preheat channel 70, the secondary reforming zone initially heats the feed indirectly with the reaction section of the secondary reforming channels 72. The primary reforming feed after heat exchange enters the primary reforming channel for reaction therein. Heat from the reaction in the secondary reforming channel 72 heats the primary reforming reaction zone in a lower portion of channel 74 as the feed passes upwardly therethrough. The effluent from the primary reaction zone continues to receive heat from the upper portion of channels 72 until it exits channels 74 and enters the tops of secondary reforming zone channels 72 for contact with the catalyst contained therein.

The arrangement of this invention can also be particularly suited for the dehydrogenation of ethyl benzene to produce styrene. The dehydrogenation of ethyl benzene to produce styrene is well known. Paraffinic feedstocks ordinarily have from about 3 to about 18 carbon atoms. Particular feedstocks will usually contain light or heavy paraffins. A catalytic

dehydrogenation reaction is normally effected in the presence of catalyst particles comprised of one or more Group VIII noble metals (e.g., platinum, iridium, rhodium, palladium) combined with a porous carrier such as a refractory inorganic oxide. Alumina is a commonly used carrier. Dehydrogenation conditions include a temperature of from about 400° to about 900° C., a pressure of from about 0.01 to 10 atmospheres, and a liquid hourly space velocity (LHSV) of from about 0.1 to 100 hr<sup>-1</sup>. Generally the lower the molecular weight of the feed the higher the temperature required for comparable conversions. The pressure in the dehydrogenation zone is maintained as low as practicable, consistent with equipment limitations, to maximize the chemical equilibrium advantages. The preferred dehydrogenation conditions of the process of this invention include a temperature of from about 400°–700° C. and a pressure from about 0.1 to 5 atmospheres.

In a preferred application of the apparatus, the arrangement in FIGS. 1 through 4 may be modified for the dehydrogenation of ethyl benzene to styrene. In order to suit the requirements for the preferred dehydrogenation of ethyl benzene, the flow arrangement outside of the reactor would require modification to provide a different flow of reactants and external heat exchange. The schematic internals of the reactor, shown by FIGS. 2 through 4, would remain essentially unchanged except for the possible elimination of the pipe distributor 30. Ignoring then the external heat exchange portion of FIG. 1 for a description of a styrene production process, a super-heated steam stream would enter the reactor via line 16, distribution header 18, and distribution spaces 20. The distribution spaces 20 supply the super-heated steam to inlets 42 of channels 44. Downward passage of the steam through channels 44 efficiently heats the reaction channels 22 by virtue of the large surface area provided by plates 25. Manifold space 45 collects the cooled steam from the open outlets 46 of the heated channels 44.

Ethyl benzene feed enters manifold space 45 from inlet 26. Manifold space 45 redistributes the steam and mixes it with the entering ethyl benzene feed to promote the dehydrogenation reaction of the steam and ethyl benzene mixture as it passes through the inlets 23 of reaction channels 22. Some form of pipe distributor may be useful in manifold 45 to distribute the ethyl benzene feed. However, direct injection of the ethyl benzene feed into inlets 23 is not essential to the use of the apparatus for ethyl benzene dehydrogenation. The reaction channels 22 contain an ethyl benzene dehydrogenation catalyst. Catalyst material may again reside in the channels as a coating applied to the plates 25 or as discrete particles retained in the channels by an appropriate screen material across inlets 23. Indirect heating across plates 25 compensates for the cooling effect of the endothermic dehydrogenation reaction as the ethyl benzene and steam mixture passes up reaction channels 22.

A collection space 24 collects the dehydrogenation zone product stream from the outlets 27 of channels 22. The manifold 48 gathers the collected reactor effluent mixture of styrene, ethyl benzene, and steam and transfers it into the product line 14 for recovery of product components and recycle of reactants and steam. The effluent stream from the dehydrogenation zone generally will contain unconverted dehydrogenatable hydrocarbons, hydrogen, and the products of dehydrogenation reactions. This effluent stream is typically cooled and passed to a hydrogen separation zone that separates a hydrogen-rich vapor phase from a hydrocarbon-rich liquid phase. Generally, the hydrocarbon-rich liquid phase is further separated by means of either a suitable selective adsorbent, a selective solvent, a selective reaction

or reactions or by means of a suitable fractionation scheme. Unconverted dehydrogenatable hydrocarbons are recovered and may be recycled to the dehydrogenation zone. Products of the dehydrogenation reactions are recovered as final products or as intermediate products in the preparation of other compounds. Additional information related to the operation of dehydrogenation catalysts, operating conditions, and process arrangements can be found in U.S. Pat. No. 4,677,237; U.S. Pat. No. 4,880,764 U.S. Pat. No. 5,043,500 and U.S. Pat. No. 5,087,792; the contents of which are hereby incorporated by reference.

A variety of other combinations of channel functions can be combined in single pass or multiple pass arrangement. The use of a plate heat exchange reactor facilitates arrangement of heat exchange channels in a wide degree of desired functionality in either single or multiple stack arrangements.

For example, the upper and lower sections of channels 74, shown as theoretically separated across catalyst loading line 96, may be readily separated physically into two separate reaction zones. Collection and distribution manifolds similar to those shown in FIGS. 1-4 and 7 and 8 can internally communicate fluid streams between the sections of separated channels. More usefully, the manifold arrangements may be used to externally communicate reaction channels contained in a single reaction vessel. External communication will facilitate control of gas streams to the different reaction zones and heat exchange zones. External control will also permit a wide variety of flow paths to be provided between the different channel arrangements.

In the way of further illustration, FIGS. 9 and 10 are charts showing a coding for possible arrangements of channel functions across a plurality of channels defined by plate elements. In addition to the codes RC, HR, RP, and RH of FIGS. 7 and 8, charts 10 and 11 of FIGS. 9 and 10 include other codes. "TC" indicates a channel that contains an additional process fluid for providing temperature control to the channels containing the reactants or the reaction effluent. "HT" designates a channel that withdraws heat from one channel section and supplies heat to another channel section. "EC" stands for a channel where the effluent from the exothermic reaction zone undergoes cooling. "R" designates a reaction zone where there is no substantial heat exchange in the reaction zone.

FIG. 9 depicts three cases of configurations for interconnecting parallel channels in a repeating pattern of functions. Case 1 of FIG. 10 represents the arrangement of channels similar to FIGS. 1-4 where the heating of reactants for the exothermic reaction takes place in alternate HR and RC channels that are located next to each other. Case 2 represents an arrangement that adds an additional preheat channel in between each reactant heating channel and in a counter-flow arrangement therewith to provide additional heat exchange of the reactants before entering the exothermic reaction channels. Case 3 adds a channel TC between the reaction channels to allow temperature adjustment for the exothermic reaction zone. In most cases the TC channels will independently circulate a fluid stream for removing additional heat from the exothermic reaction channels. Case 4 illustrates the use of a separate reaction space for the exothermic reaction with indirect heat exchange between the hot effluent and the entering feed to supply and recover heat associated with the reaction zone. In such an arrangement the catalyst for the exothermic reaction may be located in the manifold section that communicates the channels.

FIG. 10 represents further arrangements wherein multiple stacks of channels are interconnected externally or internally in a manner that provides different channel functions. All of

the configurations in the chart of FIG. 10 are simplified representations of arrangements where the reactants pass through separate upper and lower sections of heat exchange channels. A suitable manifold section can interconnect the upper and lower manifold sections to provide the necessary communication of fluids. The manifold sections may also provide convenient locations for the addition or withdrawal of supplementary fluids.

Case 5 of FIG. 10, shows a two pass exchanger section. The relatively cold reactants enter the process through the upper channels RP for preheating the reactant. After preheating the reactants then pass into the lower portion of the channels for further heating of the reactants. As indicated by the arrows, a manifold space directs the heated feed into the lower exothermic reaction channels which releases heat into the channels for heating the reactants in channels HR. The exothermic reaction zone effluent passes upwardly into the effluent cooling channels EC that provide heat for the reactant preheat section.

Case 6 of FIG. 10 representatively illustrates another two channel group arrangement that differs from Case 5 by indirectly exchanging heat across common plates of the preheat channels and the reactant channels RC while cooling the effluent from the exothermic reaction zone against the common plates of the heated channels HR. The countercurrent flow offered by this arrangement places the coldest entering reactants directly opposite the reaction zone and the hottest exiting effluent against the reacted channels. External piping can connect the HR channels with the RC channels.

Case 7 of FIG. 10 shows a variation where an internal or external heat transfer fluid carries the heat from the heated channels to the reaction channels via the heat transfer channels HT. In this arrangement the fluid in the HT channels may be an independently circulated fluid or it may be one of the reactants that is circulated in a manifold arrangement via the dotted lines that schematically represent a manifold.

Further enhancement of temperature control may be obtained by using intermediate injection of the oxidation fluid or additional fuel. Operating with a countercurrent or concurrent flow of the primary reactants leaves the sides of the channels available for cross flow injection of intermediate oxidation fluid or feed. A cross flow pattern provides an additional control on the generation of heat at specific locations thereby allowing adjustment of the temperature profile in the secondary reforming zone. Where the secondary reforming zone exchanges heat directly against the primary reforming zone, intermediate injection can also be used to influence the temperature profile within the primary reforming zone.

What is claimed is:

1. A process for contacting reactants with a catalyst in a reaction zone while indirectly heating the reactants and cooling the reaction zone by indirect heat exchange, the process comprising:

- passing a reactant-containing stream through a plurality of narrow heated channels defined by at least a first portion of spaced apart plates to heat the reactant-containing stream and to produce a heated reactant stream, at least a portion of the heated channels containing a catalyst for the promotion of an endothermic reaction;
- passing the heated reactant stream as a reaction stream to a reaction zone and contacting the reaction stream with a catalyst material for the promotion of an exothermic reaction in the reaction zone to produce a reacted stream;

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- c) indirectly heating the reactant-containing stream in the heated channels by indirect heat exchange with the reaction stream or the reacted stream across the spaced apart plates;
  - d) communicating common ends of at least two channels defined by the spaced apart plates in a common manifold; and,
  - e) collecting at least a portion of the reacted stream downstream of channels defined by a second portion of the spaced apart plates.
2. The process of claim 1 wherein the spaced apart plates define continuous channels.
3. The process of claim 1 wherein the second portion of the spaced apart plates define a plurality of narrow reaction channels to provide the reaction zone.
4. The process of claim 3 wherein the heated channels pass the heated reactant stream into a downstream portion of continuous channels that defines at least a portion of the reaction channels.
5. The process of claim 3 wherein the heated channels communicate with the reaction channels across an open chamber to pass at least a portion of the reactant-containing stream from the heated channels to the reaction channels as at least a portion of the heated reaction stream.
6. The process of claim 3 wherein heat from the reaction channels transfers to the heated channels through a temperature adjusting fluid.
7. The process of claim 6 wherein the temperature adjusting fluid undergoes heating or cooling in addition to indirect heat exchange with the reaction and heated channels to adjust the temperature conditions within the reaction zone.
8. A process for contacting reactants with a catalyst in a reaction zone while indirectly heating the reactants and cooling the reaction zone by indirect heat exchange with the reaction zone, the process comprising:
- a) passing a reactant-containing stream through a plurality of narrow heated channels defined by at least a portion of principally spaced apart plates to heat the reactant-containing stream;
  - b) passing a heated reactant stream to a plurality of narrow reaction channels defined by another portion of the spaced apart plates and containing a catalyst material therein;

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- c) indirectly heating the reactant-containing stream in the heated channels by indirect heat exchange across the portion of the spaced apart plates that defines the reaction channels to simultaneously cool the reaction channels;
  - d) communicating common ends of the narrow heated channels with the reaction channels across an open chamber at one end of the reaction and heated channels to pass at least a portion of the reactant-containing stream from the heated channels to the reaction channels as at least a portion of the heated reaction stream;
  - e) mixing an additional reactant with the reactant-containing stream in the chamber; and,
  - f) collecting a primary effluent stream from the reaction channels.
9. The process of claim 8 wherein the additional reactant stream comprises an oxygen-containing stream.
10. The process of claim 8 wherein the plates define alternate reaction channels and cooling channels.
11. The process of claim 8 wherein a containment vessel holds the plates defining the heated channels and reaction channels and a cooling medium circulates between the inside of the containment vessel and the outside of the plates.
12. The process of claim 11 wherein the cooling medium comprises the reactant-containing stream.
13. The process of claim 8 wherein the plates define corrugation and the corrugations maintain the spacing of the plates.
14. The process of claim 8 wherein the catalyst in the reaction channels comprises a particulate material retained in the channels.
15. The process of claim 8 wherein the reaction channels have an average width of less than 1 inch.
16. The process of claim 8 wherein at least one of an intermediate heated chamber communicates the heated channels with an upstream plurality of narrow channels or an intermediate reaction chamber communicates the reaction channels with a downstream plurality of narrow channels.

\* \* \* \* \*



US006409976B1

**(12) United States Patent**  
**Poschmann et al.****(10) Patent No.: US 6,409,976 B1**  
**(45) Date of Patent: Jun. 25, 2002****(54) REACTOR WITH POROUS HOLLOW FIBERS FOR CHEMICAL REACTIONS****(75) Inventors:** Thomas Poschmann, Ulm; Steffen Wieland, Stuttgart, both of (DE)**(73) Assignee:** DaimlerChrysler AG, Stuttgart (DE)**(\*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.**(21) Appl. No.:** 09/244,121**(22) Filed:** Feb. 4, 1999**(30) Foreign Application Priority Data**

Feb. 4, 1998 (DE) ..... 198 04 286

**(51) Int. Cl.:** F28D 21/00; B011 8/02**(52) U.S. Cl.:** 422/199; 422/196; 422/198; 422/312**(58) Field of Search** ..... 48/198.6-198.7; 48/198.8, DIG. 5; 422/199, 196, 206, 197, 312, 236, 238, 239, 218, 220, 221, 240, 174, 95/45, 56, 55; 96/10; 392/488**(56) References Cited****U.S. PATENT DOCUMENTS**

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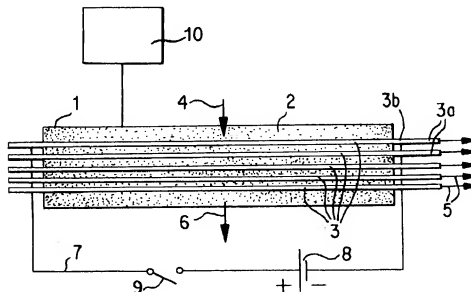
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**(57) ABSTRACT**

A reactor for the catalytic chemical reaction of a gaseous or liquid reaction starting product to a reaction end product that contains a gaseous or liquid reaction constituent which can be selectively separated by means of a membrane diffusion includes a reaction space into which the reaction starting product flows and which contains a suitable catalyst material. Porous hollow fibers are placed in the reaction space as membranes for the selective separation of the reaction constituent from the residual reaction end product.

**9 Claims, 1 Drawing Sheet**

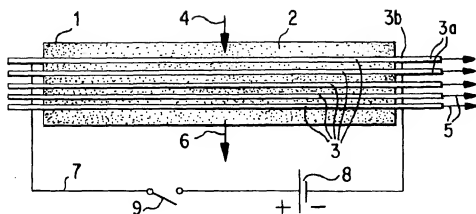


Fig. 1

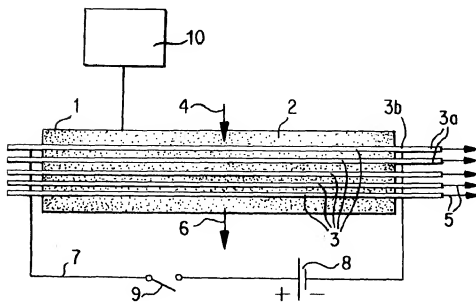


Fig. 2



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# REACTOR WITH POROUS HOLLOW FIBERS FOR CHEMICAL REACTIONS

## BACKGROUND AND SUMMARY OF THE INVENTION

This application claims the priority of German Patent Application No. 198 04 286.8, filed Feb. 4, 1998.

The present invention relates to a reactor for the catalytic chemical reaction of a gaseous or liquid starting product to an end product that contains a gaseous or liquid constituent which can be selectively separated by means of membrane diffusion.

Reactors which are suitable for the catalytic chemical reaction of a gaseous or liquid reaction starting product to a reaction end product, wherein the reaction end product contains a gaseous or liquid reaction constituent that can be selectively separated by means of membrane diffusion, are in use, for example, for the water vapor reforming of methanol. Such reactors have a reaction space into which the reaction starting product can flow and which contains a suitable catalyst material. In the water vapor reforming of methanol, a hydrogen-rich mixture containing a certain part of carbon monoxide is obtained as the reaction end product. It is known to use such methanol reforming reactors in mobile systems in fuel-cell-operated motor vehicles in order to obtain the hydrogen required for the fuel cells from liquid methanol. Since carbon monoxide has a damaging influence on the fuel cells, the reaction end product of the methanol reforming reaction requires a corresponding treatment. The selective separation of the hydrogen by means of a membrane diffusion is known as one possibility. Particularly for a mobile use in automotive engineering, it is desirable for reasons of dynamics and space that the reactor have a construction which is as compact and as light as possible and has few components. In this case, as few control units and automatic control units as possible should be used, while a high efficiency is simultaneously endeavored.

U.S. Pat. No. 4,981,676 discloses a reactor which is used for the water vapor reforming of a hydrocarbon, particularly methane, and contains a cylindrical-ring-shaped reaction space that is filled with a suitable catalyst pellet charge. To the outside, the reaction space is bounded by a metallic wall which can be heated from the outside, while the inner boundary of the reaction space is formed by a tube that acts as a hydrogen separating membrane and has a correspondingly porous ceramic tube wall. The diameter of the membrane tube is typically of the order of 25 mm and greater.

European Patent Document EP 0 228 885 B1 discloses a reactor for the decomposition of hydrogen sulfide for the purpose of obtaining hydrogen, which is constructed as a so-called tube bundle reactor. The reactor contains a bundle of spaced reaction tubes which form the reaction space. The reaction tubes are implemented by means of a porous wall such that they act as a selectively hydrogen-separating membrane as well as contain a suitable catalyst material. The wall thickness of the tube is approximately 1 mm and the tube diameter is a multiple thereof.

As a special membrane for the selective separation of certain constituents from a substance mixture by means of membrane diffusion, so-called hollow fibers are known, as described, for example, in European Published Patent Application EP 0 186 129 A2 and U.S. Pat. Nos. 4,175,153, 5,474,680, and 5,558,936. These hollow fibers have a porous wall made, for example, of ceramic or glass material, through which one selected constituent of a substance mixture can move. Such hollow fibers are suggested, for

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example, for the selective separation of hydrogen from a hydrogen-containing mixture. The hollow fibers typically have a diameter of the order of several hundredths of a millimeter to a few millimeters and wall thicknesses of the order of 1  $\mu\text{m}$  to a few 100  $\mu\text{m}$ . U.S. Pat. No. 4,175,153 specifically discloses a hydrogen separating stage with a cylindrical housing in which a bundle of such hollow fibers is placed in a mutually spaced manner. The hydrogen-containing mixture, such as the reaction end product of a water vapor reforming of methanol, is introduced into the housing on the face side and is guided through the interior of the hollow fibers arranged in parallel. The hydrogen is selectively diffused through the hollow fiber walls and, as the result, is separated from the remaining mixture constituents. U.S. Pat. No. 4,175,153 discloses, as a further application possibility, the use of such hydrogen-permeable hollow fibers as a fuel cell electrode in a fuel cell or in catalyst-filled hydrogen-generating reactors. A hydrogen generating reactor with several small thin hollow diffusion tubes which traverse a catalyst bed is disclosed in Austrian Patent Document AT 247 284.

One object of the present invention is to provide a reactor that can be constructed in a relatively compact and easy manner.

Another object of the invention is to provide a reactor that permits a high reaction efficiency.

Still another object of the invention is to provide such a reactor which, during a cold start, permits a fast heating of its membrane-type hollow fibers to an operating temperature suitable for the effective reaction constituent separation.

These and other objects and advantages are achieved by the reactor according to the invention, in which porous hollow fibers are placed directly in the reaction space and operate there as membranes for the selective separation of a selectively separable constituent contained in the reaction end product from the residual reaction end product. In this case, the constituent of the reaction end product formed in the reaction space which is to be separated, diffuses from the reaction space through the porous hollow fiber wall into the inner duct of the respective hollow fiber, and can be withdrawn from the reaction space by way of the hollow fiber ducts. The separating membranes are therefore situated directly at the site at which the catalytic chemical reaction takes place and permit a separation of the concerned constituent, such as hydrogen, from a hydrogen-containing mixture, with high selectivity and yield. By the separation of this constituent while at the site of the chemical reaction, the reaction equilibrium can be displaced to the side of the desired constituent.

The positioning of the membrane-type hollow fibers in the reaction space itself benefits a compact reactor construction, and by the use of membrane-type hollow fibers, in the case of a given constructional volume, a comparatively high membrane surface area can be made available for the diffusive separation of the desired constituent. The compact reactor construction with hollow-fiber separating membranes integrated in the reaction space has a favorable effect on achieving fast reaction times under fluctuating load conditions. This makes the reactor particularly suitable for motor vehicles, where transient operating phases occur frequently. In particular, the reactor can be used as a methanol reforming reactor for obtaining hydrogen by the water vapor reforming of methanol in fuel-cell-operated motor vehicles.

The porous hollow fibers are constructed of a ceramic or glass material and are provided with a selectivity-increasing

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metallic coating. The metal material of this coating is selected such that the selectivity of the separation of the desired reaction constituent is increased. Furthermore, devices are provided for heating the porous hollow fibers by applying an electric voltage to their metallic coating. This arrangement heats the hollow fibers in a simple manner, so that, for example, during a starting phase, they can very rapidly be brought to a raised temperature required for an effective separating function.

In the case of a reactor according to another embodiment of the present invention, the catalyst material is present in a catalyst layering which is formed by (1) a catalyst pellet charge; (2) a porous carrier body, into which the catalyst material is charged; or (3) a metallic foam catalyst body that consists of the mostly metallic catalyst material. The porous hollow fibers extend in a parallel arrangement with a pre-determined mutual transverse spacing through the catalyst layering.

Other objects, advantages and novel features of the present invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic longitudinal sectional view of a reactor which can be used, for example, for the water vapor reforming of methanol; and

FIG. 2 is a schematic view of a reactor and heat source for the reaction space.

#### DETAILED DESCRIPTION OF THE DRAWINGS

The reactor illustrated in the schematic longitudinal sectional view of the figure contains a reaction space 1 into whose interior a catalyst layering 2 is charged. The catalyst layering 2 contains a catalyst material suitable for carrying out the intended catalytic chemical reaction, for example, a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-material for the case of a water vapor reforming of methanol. The catalyst layering 2 may be formed by (1) a catalyst pellet charge; (2) a porous, carrier body of a ceramic material, of glass, carbon or plastic, into whose pores the catalyst material is charged; or (3) a metallic foam body containing a metal which catalyzes the desired chemical reaction.

In a conventional manner, which is therefore not shown in detail, a gaseous or liquid reaction starting product 4 can be introduced into the reaction space 1 and can be converted there by a corresponding catalytic chemical reaction to a reaction end product that contains a gaseous or liquid constituent 5 which can be separated by means of membrane diffusion. In particular, the reactor can be used in a fuel-cell-operated motor vehicle for obtaining hydrogen for the fuel cells by means of a water vapor reforming of liquid methanol. The reaction starting product 4 is a prepared water vapor/methanol mixture. In this case, the reaction end product is a hydrogen-rich mixture which includes a certain part carbon monoxide and is therefore not suitable for direct feeding into the fuel cells.

Characteristically, hollow fibers 3 are placed in the reaction space 1 as membranes for the selective separation of a desired reaction constituent of the reaction end product formed by the reaction in the reaction space 1. Typical diameters of the hollow fibers 3 are in the range of between tens of micrometers to several millimeters and in the case of wall thicknesses in the range of from approximately 1  $\mu$ m to several 100  $\mu$ m. As a bundle and spaced in parallel from one

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another, the hollow fibers 3 extend through the reaction space 1 and penetrate the catalyst layering 2. They are of a construction and a composition which is known per se for this purpose and are selected as a function of the reaction constituent 5 which is to be selectively separated so that only this constituent, and not the other constituents of the reaction end product, can diffuse through the hollow-fiber wall in the inner duct 3a of the respective hollow fiber 3, from which it can be withdrawn from the reaction space.

In the above-mentioned technique for obtaining hydrogen by the water vapor reforming of methanol in fuel-cell-operated motor vehicles, the hollow fibers 3 are constructed to be correspondingly selectively hydrogen-permeable so that the hydrogen is separated from the residual constituents of the reaction end product in an extremely pure form and can be discharged by way of the interior ducts 3a of the hollow fibers 3 from the reaction space 1 and can be fed to the fuel cells. The residual reaction end product 6 is discharged in a conventional manner, which is not shown, from the reaction space 1. As schematically illustrated in the figure, the main flow direction of the reaction starting product 4 guided through the reaction space is selected to be perpendicular to the longitudinal direction of the hollow fibers 3.

If the carrying-out of an endothermic reaction is intended, as is the case during the water vapor reforming of methanol, the required heat is provided to the catalyst layering 2 in a conventional manner. Examples of heating the catalyst layer include external heating 10 of the reaction space or causing a preferably catalytic combustion operation in the reaction space 1, for example, with the additional feeding of oxygen, which permits an exothermal partial oxidation reaction.

In order to increase the separating selectivity of the hollow fibers 3 with respect to the reaction constituent to be separated, the hollow fibers 3 are provided with a metallic layer 3b, on the exterior side, or as an alternative on the interior side. Metals of the groups IVb, Vb and VIII as well as their alloys or fine-pored ceramics therefrom are suitable for this purpose.

In addition, the metallic coating 3b of the hollow fibers 3 can be utilized for a rapid heating of the porous hollow fibers 3. For this purpose, the metallic coatings 3b of the individual hollow fibers 3 are connected electrically in parallel to a heating circuit 7 which is shown only schematically and which contains a voltage source 8 and a controllable switching element 9 for switching the heater on and off. The hollow fibers 3 are in each case connected by means of their metallic layer 3b on the end side with a respective pole of the heating voltage source 8 so that, when the switch 9 is closed, a heating current flows through the metallic layers 3b and generates ohmic heat there. As a result, the hollow fibers can be heated during a starting phase within a few seconds, to a temperature which is above the ambient temperature, at which the diffusion of the constituent which is selectively separated, such as the hydrogen of a hydrogen-rich reformate gas mixture, takes place with sufficient effectiveness.

The control of the functions specifically mentioned above as well as of the other customary reactor functions is carried out by a suitable reactor control device which is not shown and which is designed correspondingly, which is obvious to a person skilled in the art.

It is also understood that, in addition to the illustrated example, further implementations of the reactor according to the invention are conceivable, in which case reactors according to the invention can be used not only, as described, for the water vapor reforming of methanol but for other catalytic

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chemical reactions in which a gaseous or liquid reaction starting product is reacted in a reaction space to a reaction end product which contains a gaseous or liquid reaction constituent which can be selectively separated by means of the porous membrane-type hollow fibers. In this case, arbitrary constructions of the reaction space are conceivable in which the hollow fibers are placed in a suitable number and arrangement.

The foregoing disclosure has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.

What is claimed is:

1. A reactor for the catalytic chemical reaction of a gaseous or liquid reaction starting product to a reaction end product that contains a gaseous or liquid reaction constituent which can be selectively separated by means of membrane diffusion, comprising:

a reaction space into which the reaction starting product flows;

a catalyst material disposed in the reaction space;

porous hollow fibers disposed in the reaction space, said porous hollow fibers being made of a material which is selectively permeable to said gaseous or liquid reaction constituent, for separation of the gaseous or liquid reaction constituent from the reaction end product by diffusion thereof through walls of said porous hollow fiber, from said reaction space into an interior space of said porous hollow fibers;

a metallic coating on each of the porous hollow fibers;

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a device that heats the porous hollow fibers during a starting phase to an operating temperature at which selective diffusion of the reaction end product occurs by applying an electric voltage to the metallic coatings; and

a separate heat source that heats the catalyst material in the reaction space.

2. A reactor according to claim 1, wherein the catalyst material in the reaction space comprises catalyst pellets.

3. A reactor according to claim 1, wherein said hollow fibers comprise a ceramic material or a glass material.

4. A reactor according to claim 1, wherein the catalyst material in the reaction space is a metallic foam body and said porous hollow fibers extend through said metallic foam body.

5. A reactor according to claim 4, wherein said hollow fibers extend through said metallic foam body in an equally spaced manner.

6. A reactor according to claim 1, wherein the catalyst material is in the pores of a carrier body made of a material selected from the group consisting of ceramic, glass, carbon and plastic.

7. A reactor according to claim 1, wherein said catalyst material comprises a compound comprising Cu, ZnO, Al<sub>2</sub>O<sub>3</sub> and combinations thereof.

8. A reactor according to claim 1, wherein said metallic coatings comprise a metal, metal alloy or ceramic comprising an element selected from the group consisting of Group IVb, Group Vb and Group VIII of the periodic table of elements.

9. A reactor according to claim 1, wherein the separate heat source is an external heat source.

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